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CCXXX.—*The System Ferric Oxide–Arsenic Acid–Water at Low Concentrations of Arsenic Acid.*

By Norman Holt Hartshorne.

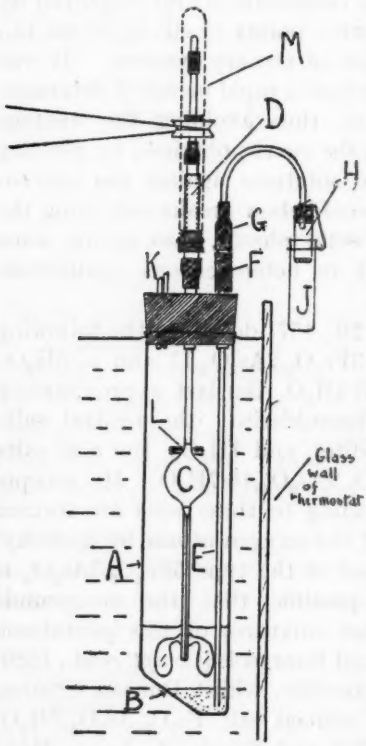
This work was undertaken (*a*) to discover whether any of the numerous ferric arsenates described in the literature were merely stages in a series of adsorption compounds, as in the case of the ferric phosphates (Carter and Hartshorne, J., 1923, **123**, 2223); and (*b*) to test the usefulness of the viscometer-stirrer employed by the author to determine the transition points of salt hydrates (J., 1924, **125**, 2097) in the investigation of ternary systems. It was thought that this apparatus would afford a rapid means of determining the attainment of equilibrium, thus avoiding the wastage involved in test analyses, and that the curves obtained by plotting the time of flow of the saturated solutions against the concentration of one of the components would show breaks indicating the limits of stability of the various solid phases, thus saving some of the laborious analyses inherent in heterogeneous equilibrium work.

Metzke (*Z. anorg. Chem.*, 1899, **19**, 457) describes the following ferric arsenates: The basic salts, $3Fe_2O_3,2As_2O_5,17$ and $16{\cdot}5H_2O$; $4Fe_2O_3,3As_2O_5$, 33·5, 20·5, and $15{\cdot}4H_2O$, the last approximating to the naturally occurring pharmacosiderite; the neutral salts $Fe_2O_3,As_2O_5,10,9,4$ (artificial scorodite), and $1H_2O$; the acid salts $2Fe_2O_3,3As_2O_5,22{\cdot}5H_2O$ and $Fe_2O_3,3As_2O_5,16{\cdot}7H_2O$. He accepts the view that the acids corresponding to these salts are formed from As_2O_5 by the replacement of the oxygen atoms by hydroxyl groups. On this basis, a compound of the type $5Fe_2O_3,3As_2O_5$ is missing, but Metzke thinks it possible that the compounds $3Fe_2O_3,2As_2O_5,17$ and $16{\cdot}5H_2O$ are mixtures of this pentabasic salt with one less basic. Verneuil and Bourgeois (*Compt. rend.*, 1880, **90**, 223) also prepared artificial scorodite, whilst Duncan (*Pharm. J.*, 1905, **20**, 223) describes the neutral salt $Fe_2O_3,As_2O_5,2H_2O$, which is dehydrated at 100°. Ježek and Siměk (*Z. Kryst. Min.*, 1914, **54**, 88) state that an anhydrous neutral salt is formed as a deposit of black prismatic crystals in the Deacon chlorine process. Other ferric arsenates, most of which approximate to those given above, are described by workers in the early part of the last century, notably Berzelius, but the inaccurate analytical methods available at that time and the exhaustive nature of Metzke's researches make it unnecessary to specify them. The following ferric arsenates occur in nature: pharmacosiderite, $4Fe_2O_3,3As_2O_5,15H_2O$; white iron-sinter, $2Fe_2O_3,As_2O_5,12H_2O$; and scorodite, $Fe_2O_3,As_2O_5,4H_2O$.

EXPERIMENTAL.

The system was studied at 25°. The apparatus used for preparing the equilibrium mixtures and collecting the phase samples is shown in Fig. 1. The solubility tube, A, was about 6 cm. wide and 26 cm. long, having a bottom so shaped as to collect the solid at the foot of the tube, E. This shape is very useful when (as was often the case in the present investigation) the amount of solid is small. It is important that the sloping portion, B, should be sufficiently steep. The viscometer-stirrer, C, was the same as that used in the previous work (*loc. cit.*), *i.e.*, with a capillary diameter of about 0·75 mm. It was supported by a glass bearing with thrust surfaces ground to a good fit and packed with vaseline contained in the tube, D. This type of bearing is simple to make, trustworthy, and sufficiently air-tight in cases where rigorous sealing of the solubility tube is unnecessary. Any vaseline which ran down the stem of the viscometer was caught by the rings of filter paper at L. These were changed occasionally and were quite effective in preventing contamination of the mixtures. The apparatus for collecting the phase samples is shown connected to the solubility tube by means of the rubber tube, F (which normally was closed by a piece of glass rod), and the sliding connexion, G. It consisted of the collecting tube, E, the weighed filter, H, and the weighing bottle, J, being thus merely a modification of the apparatus used previously for ferric and ferrous phosphates (*loc. cit.*; Carter and Hartshorne, J., 1926, 363), the most important difference being that it was not now necessary to filter the samples at thermostat temperature, since this was not far removed from that of the room. Dry air for forcing the samples through the filter was admitted through the tube, K. During this operation,

FIG. 1.



the stirrer bearing was sealed by the tube, M, after removal of the pulley. The samples were subsequently dissolved in hydrochloric acid and diluted to a standard volume. The solubility tube was supported in a glass-sided thermostat maintained at 25° ± 0·02° by means of an ordinary gas regulator.

Some difficulty was experienced in finding a suitable starting point for the preparation of the equilibrium mixtures. Arsenic acid ($H_3AsO_4,\frac{1}{2}H_2O$) was prepared by the oxidation of A.R. arsenious oxide (B.D.H.) according to the method described in Vanino's "Präparative Chemie," 1921, Vol. I, p. 215. Ferric hydroxide, prepared by the method used in the ferric phosphate work, could not, however, be dissolved in a solution of the arsenic acid; in spite of many variations in the conditions, only very small proportions were attacked. This is no doubt to be attributed to the small solubility of the ferric arsenates in arsenic acid, for in some cases microscopic examination showed that the ferric hydroxide particles were coated with arsenate, which prevented further action. It has been found that in solutions containing up to 22% of As_2O_5 the solubility at 25° never exceeds 0·1% of Fe_2O_3. The difficulty was eventually overcome by adding hydrochloric acid to the mixture. The ferric chloride thus formed reacted with the arsenic acid, and on repeated evaporation to dryness the ferric arsenate was freed from all but a trace of hydrochloric acid. The mixture, especially when concentrated, had a greenish-blue tint. On one occasion after an evaporation disc-shaped particles separated similar to those observed by Metzke (*loc. cit.*) when attempting to prepare artificial scorodite. The greenish-blue colour of these and other preparations is also mentioned by Metzke and is evidently due to a complex ferriarsenic acid or acids, analogous to the pink ferriphosphoric acids. This view is supported by the observations of Metzke and earlier workers, that the neutral and acid arsenates dissolve in concentrated ammonia, and by that of Duncan (*loc. cit.*), that oxidised solutions of ferrous arsenates respond very faintly to the thiocyanate test for ferric iron.

The mixture thus prepared was the basis of all the equilibrium mixtures studied. A portion, suitably diluted with water and freed from large lumps of solid, was transferred to the solubility tube, and after equilibrium had been reached and the necessary phase samples collected, water or syrupy acid was added and a new equilibrium reached, and so on.

Some difficulty had been anticipated in keeping the capillary of the viscometer clean. The method of washing with a few drops of water cannot be used in ternary systems of the present type, since the addition of water in large excess to most of the saturated

solutions results in the precipitation of neutral or basic salts. In the present work, a dilute solution of arsenic acid was found quite satisfactory as a wash liquid, and a few drops of this were blown down the viscometer from a wash-bottle every time the composition of the mixture was changed. Such a procedure was neither permissible nor necessary in order to obtain concordant results for successive readings of the same equilibrium. In order to provide for cases in which suitable wash liquids cannot be found for a ternary system, the author has devised an apparatus in which the stirrer and viscometer are separate, the latter being instantly removable for cleaning without disturbing the rest of the apparatus. So far, however, it has been found quite unnecessary to use it. Moreover, in ternary systems the temperature is kept constant, and consequently crystallisation in the capillary through temperature changes cannot occur. When readings are being taken with the viscometer, it is essential that the air expelled from the solubility tube by the falling liquid should be able to escape easily. In the previous work, the stirrer bearing provided an adequate leak, but in the present case it was found necessary to remove the glass plug from the tube, F (Fig. 1). When equilibrium was established the readings agreed to within 0·4 sec., and frequently to within 0·2 sec. The agreement is closer than in the previous work, but the percentage error remains about the same.

The analysis of the phase samples was effected as follows. The arsenic was separated by reduction with hydrazine and subsequent distillation as arsenious chloride. The apparatus used was that described by Jannasch and Seidel (*Ber.*, 1910, **43**, 1218), with the addition that the receiver was cooled in a large beaker of water and was furnished with a water trap to prevent any escape of arsenic. (These precautions are, however, probably unnecessary.) An aliquot part of the phase sample solution was measured into the distillation flask, concentrated hydrochloric acid was added until the volume was about 110 c.c., and the solution was saturated with hydrogen chloride; 3 g. of hydrazine sulphate and 1 g. of potassium bromide were then added, and the liquid was distilled until only 30—40 c.c. remained. The distillate was titrated as described below. High results are obtained unless the flame is screened from all but the bottom of the flask by an asbestos ring with a wire gauze centre: without this precaution, the flask becomes heated above the liquid and hydrazine distils over. The amount of arsenic in the reagents was found to be negligible. The use of a continuous stream of hydrogen chloride during the distillation was found, in agreement with Jannasch and Seidel, to be quite unnecessary for the complete volatilisation of the arsenic.

The distillate was titrated with potassium iodate solution, according to the method described in Scott's "Standard Methods of Chemical Analysis," 1922, Vol. I, p. 44. The iodate solution was standardised against resublimed A.R. arsenious oxide (B.D.H.). Owing to the distillation, the arsenious chloride solution was more dilute than is usual in this titration, and the reaction was consequently slower; it was therefore necessary to add the last few c.c. of the iodate very cautiously, waiting 5 minutes between each addition. As a check, the solution was titrated back with a standard arsenite solution, but the first drop almost invariably restored the colour to the chloroform.

The iron in the liquid phase was determined colorimetrically with ammonium thiocyanate—it never exceeded 0·1% as Fe_2O_3. In the solid phases, it was determined either (1) gravimetrically as oxide in the residue from the arsenic distillation, after decomposing the excess of hydrazine with nitric acid; (2) by titration of the residue with potassium dichromate, after removing the hydrazine with nitric acid and expelling the latter by evaporation; or (3) by direct titration of the phase sample solution with potassium dichromate. Stannous chloride was used as a reducing agent in the dichromate titrations. Methods (1) and (2) were both unsatisfactory because the weights of iron in the quantities of solution necessary to obtain a convenient amount of arsenious chloride were small. By using method (3) more solution could be titrated, and it was found by experiment that, provided the concentration of hydrochloric acid was not too high, the presence of the small amounts of arsenate involved did not appreciably affect the results. To ensure that the hydrochloric acid concentration was sufficiently low, the phase sample solutions were diluted with water before reduction by the stannous chloride, until in the cold the colour due to the ferric chloride was a pale yellow.

Results.

The results are in Table I. The composition of the phases is expressed in terms of Fe_2O_3 and As_2O_5, and, in the case of mixtures 1—13, as $FeAsO_4$ and H_3AsO_4 also. This second mode of expression is made possible by the absence of basic solid phases, and its object is to bring out more clearly the orientation of the conjugation lines when the results are plotted. If Fe_2O_3 and As_2O_5 are used as plotting components, the diagram is confined within an area which is very narrow in the direction $Fe_2O_3 \longleftrightarrow As_2O_5$, and its significance is difficult to appreciate. Mixtures 14—20 are not so treated because their percentages of Fe_2O_3 in the liquid phase were only determined approximately. Graphic expression is, however, not

TABLE I.

(Solid phase analyses marked with an asterisk refer to the *dried* solid, the remainder to the moist solid.)

	Liquid phase.					Solid phase.			
Mixture.	Time of flow (secs.).	% Fe_2O_3.	% As_2O_5.	% $FeAsO_4$.	% H_3AsO_4.	% Fe_2O_3.	% As_2O_5.	% $FeAsO_4$.	% H_3AsO_4.
1	81·7	Trace.	2·6	Trace.	3·2	10·3	17·0	25·1	2·7
2	82·6	,,	3·5	,,	4·3	10·8	18·2	26·3	3·3
3	83·4	,,	4·4	,,	5·4	9·6	17·1	23·4	4·1
4	84·5	,,	5·4	,,	6·7	13·7	23·3	33·4	4·45
5	85·0	,,	5·8	,,	7·2	10·9	20·9	26·6	6·4
6	85·7	,,	6·4	,,	7·9	15·8	27·9	38·5	6·4
7	86·6	0·001	7·96	0·001	9·83	—	—	—	—
8	89·0	0·004	10·11	0·01	12·47	4·1	15·2	10·0	11·5
9	92·1	0·01	12·49	0·02	15·40	5·5	18·74	13·4	13·4
10	97·4	0·036	16·19	0·088	19·93	—	—	—	—
11	102·0	0·037	18·82	0·090	23·17	2·7	21·22	6·6	21·41
12	108·0	0·059	21·77	0·14	26·78	3·4	24·94	8·3	24·75
13	110·6	0·076	23·13	0·185	28·42	26·8*	52·8*	65·4*	17·5*
14	87·4	Approximately 0·1	8·0			—	—		
15	87·4		8·4			—	—		
16	92·6		12·3			21·8*	58·6*		
17	94·1		13·2			—	—		
18	95·5		14·3			—	—		
19	96·7		14·9			—	—		
20	97·7		15·5			22·5*	57·9*		

Composition and Appearance of Solid Phases.—Mixtures 1—10: Fe_2O_3,As_2O_5,xH_2O, with adsorbed acid. Amorphous.

Mixtures 11—13: Fe_2O_3,As_2O_5,xH_2O (with adsorbed acid) + $Fe_2O_3,2As_2O_5,8H_2O$. Amorphous and needles.

Mixtures 14—20: $Fe_2O_3,2As_2O_5,8H_2O$ (Calc.: Fe_2O_3, 20·94; As_2O_5, 60·21%). Needles.

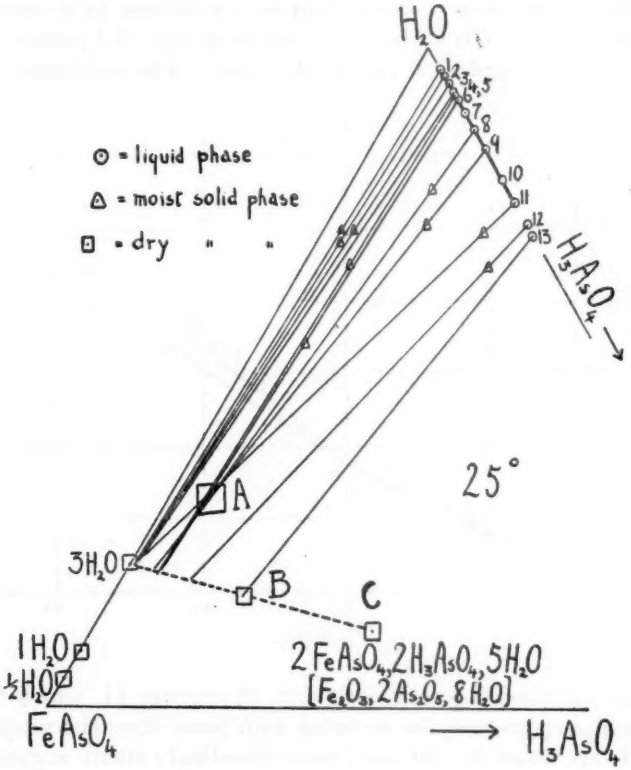
so necessary for those mixtures, for the compositions of their solid phases were found by analysis of the dried solid. Fig. 2 shows mixtures 1—13 plotted on a triangular diagram, and Fig. 3 shows the times of flow of the liquid phases (excluding mixture 13) plotted against their content of As_2O_5.

From Table I, it is seen that the percentage of ferric oxide in all the liquid phases is extremely small: even mixtures 14—20 which are metastable show only about 0·1%. It was feared at first that this small solubility would render the viscosity measurements useless through their not differing appreciably from those of aqueous arsenic acid solutions. The curves in Fig. 3 show, however, that mixtures 14—20 have a distinctly higher viscosity than the others at the same acid concentrations; on the assumption that the viscosity increases with solubility, this confirms the metastability of these

mixtures. Further, a distinct break occurs between mixtures 6 and 7, the significance of which is discussed later.

From Table I it will be seen that the mixtures 11—13 possessed the same two solid phases. It is evident that in these cases equilibrium was not attained, since theory demands that there shall be only one composition for a solution in equilibrium with any two

FIG. 2.

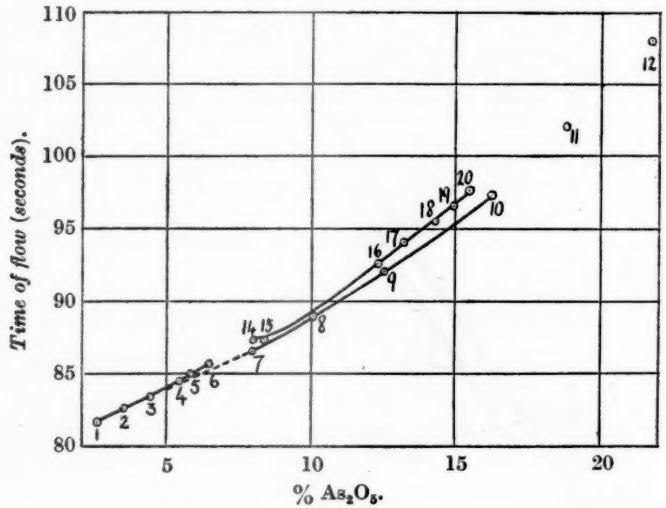


solid phases at constant temperature. This is not to be attributed to any failure to take the usual precautions to ensure the attainment of equilibrium, for the stable solid phase was presumably present in each case, and stirring was continued long after any change in the viscosity of the solution and in the appearance of the solid under the microscope had ceased (the mixtures were stirred for 35, 6, and 26 days, respectively). Rather must it be ascribed to an extreme sluggishness in approaching equilibrium. This was also experienced in the ferric phosphate work in this region, and is no doubt due to

the low solubility of the solid phases. In view of this, it is impossible to be certain to what extent equilibrium was reached in the other mixtures. The least doubt would appear to attach to mixtures 14—20 which possessed a single well-defined crystalline solid phase. These, however, were metastable.

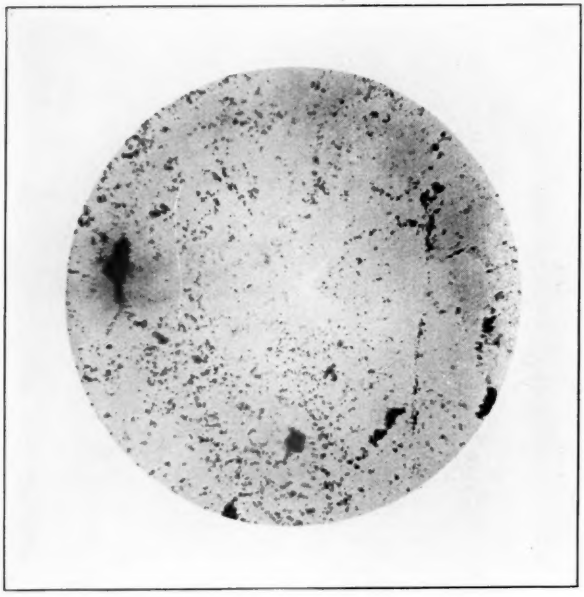
The solid phase of mixtures 1—10 was seen under the microscope to be very finely divided, the average diameter of the particles being 1·0—1·5 μ. Under crossed Nicols and an oil-immersion objective they showed no trace of colour and may therefore be described as amorphous. Fig. 4 is a photomicrograph of the solid phase of mixture 1 which is typical of the whole series. The conjugation lines

FIG. 3.



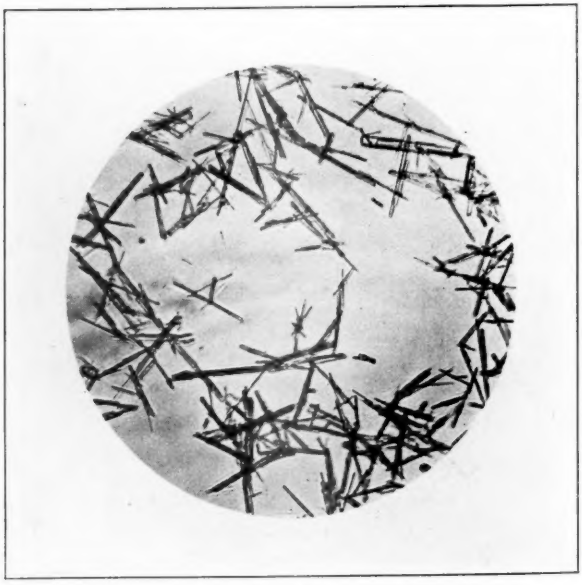
of these mixtures together with that of mixture 11, which for all practical purposes may be included with them since the proportion of acid salt which it contained was exceedingly small, suggest (see Fig. 2) that the solid is a neutral ferric arsenate containing varying amounts of adsorbed arsenic acid. In this respect the system is similar to the ferric phosphate system (*loc. cit.*). Marked adsorption is indeed to be expected in these cases, for the solid is finely divided and amorphous. This factor limits the value of any conclusions drawn from the conjugation lines, and further evidence is necessary to show where they end. In the present case an attempt to provide this was made by analysing the dried solid phase of mixture 13 (point B). This contained both the neutral arsenate and the acid salt $Fe_2O_3,2As_2O_5,8H_2O$ (point C), so that extrapolation of the line

FIG. 4.



Fe_2O_3,As_2O_5,xH_2O *and adsorbed acid.*
Average diameter of particles : **1·0—1·5** μ.

FIG. 5.



$Fe_2O_3,2As_2O_5,8H_2O$.
(× 260).

[*To face p.* 1767.]

CB gives information as to the water content of the former. As will be seen from the figure, this leads to the composition

$$FeAsO_4,3H_2O \text{ (or } Fe_2O_3,As_2O_5,6H_2O).$$

No great reliance can, however, be placed on the accuracy of the determination of the point B, since it is probable that the solid suffered some change in composition during the drying process on account of its fine state of division and the presence of adsorbed acid. (The solid was washed with anhydrous ether which was then removed in a current of dry air.)

It will be noticed that the lines fall into two groups, *viz.*, 1—4 and 5—11, the latter converging approximately on the point A. It does not appear, however, that this has any significance, for the point A is far removed from the line CB, and, moreover, no simple formula can be assigned to it. The break in the viscosity curve between mixtures 6 and 7 (see Fig. 3) may be due to a small change in the solid phase, but it is more probably due to incomplete attainment of equilibrium, especially as the order in which the mixtures were prepared was from Nos. 6 to 1 followed by a reversion to No. 7, *i.e.*, to the mixture on the other side of the break. Possibly the true course of the curve is as represented by the broken line drawn from 3 to 7.

If the conjugation lines reach as far as the line CB produced, the diagram shows that certain of them cross over the others. This, too, indicates that equilibrium was not attained, for it implies that a mixture of the three components lying within the crossing region has a choice of equilibrium states. A similar arrangement of lines was observed in the ferric phosphate work at 25° (*loc. cit.*, p. 2226), but its significance was not then appreciated. For the present, the solid phase in equilibrium with mixtures 1—10 is described as Fe_2O_3,As_2O_5,xH_2O (where x is probably not far removed from 6), containing adsorbed acid.

Mixtures 14—20 were made by stirring another portion of the starting material with arsenic acid solutions of progressively decreasing strengths. They were all metastable, as both the analyses and the viscosity curves show. The solid consisted of small needle-shaped crystals (see photomicrograph, Fig. 5) which could be easily filtered; they were dried by washing with ether and underwent no visible change. They were therefore analysed dry in two cases and the results are given in Table I. From these figures and from the crystalline form, it was concluded that they were $Fe_2O_3,2As_2O_5,8H_2O$, isomorphous with $Fe_2O_3,2P_2O_5,8H_2O$ (*loc. cit.*, p. 2230). The analytical figures are not as close to this composition as is desirable, but they do not agree with any other known or anticipated compound. The inaccuracy is probably due to the smallness

of the crystals, the relatively large surface magnifying the effect of incipient decomposition. The error is in the basic direction, which is in agreement with this explanation. This compound does not appear to have been described before. Its constitution and that of its phosphate analogue cannot be explained in any simple manner on the assumption that the salts are formed simply by the replacement of acid hydrogen by ferric iron. This is further evidence that the salts are complex. A formula analogous to that given by Weinland and Ensgraber to the phosphate would serve also for the arsenate, *viz.*, $[Fe(AsO_4)_2]H_3,2{\cdot}5H_2O$. No sign of Metzke's compound, $2Fe_2O_3,3As_2O_5,22{\cdot}5H_2O$, has been found.

Summary.

The system ferric oxide–arsenic acid–water has been studied between the concentrations 2·6 to 23·13% of As_2O_5 at 25°. Within this range the following solid phases have been found: The neutral salt, Fe_2O_3,As_2O_5,xH_2O (where x is probably not far removed from 6), carrying varying amounts of adsorbed arsenic acid; and the acid salt, $Fe_2O_3,2As_2O_5,8H_2O$, which has apparently not been described before. No basic salts were obtained. A feature of the system was the sluggishness with which equilibrium was approached even in the presence of the stable phase, and it is evident that in some cases it was not attained.

The author's stirrer-viscometer was used in this work in order to test its usefulness in the investigation of ternary systems. No difficulty was experienced in obtaining readings concordant to within 0·5% and frequently less. The system did not, however, afford much opportunity for making use of viscosity measurements.

In conclusion, the author wishes to express his thanks to Dr. J. F. Spencer for his helpful interest in this work.

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UNIVERSITY OF LONDON. [*Received, April 2nd*, 1927.]

CCXXXI.—*The Preparation and Hydrolysis of the Isomeric β-Tolylethyl Bromides.*

By JOHN BALDWIN SHOESMITH and ROBERT JORDAN CONNOR.

IN a recent paper (Shoesmith and Slater, J., 1924, **125**, 2278), comprising one of a series of investigations on the polar and other factors which govern the reactivity of halogens in substituted halogenated benzenoid derivatives, the transmission of a powerful alternating influence from the methyl group of the tolyl radical

to halogen (*a*) directly attached to the same benzene nucleus and (*b*) removed by one carbon atom from the nucleus was demonstrated by the great difference in reactivity of the halogens in the isomeric iodotoluenes, $CH_3 \cdot C_6H_4I$, and ω-bromoxylenes, $CH_3 \cdot C_6H_4 \cdot CH_2Br$, and by the manner in which the order of ease of replacement of the bromine atoms in the latter case is dependent on the reagent used.

The interesting problem as to how far the influence of the methyl group extends beyond the benzene ring has now been investigated, the isomeric β-tolylethyl bromides having been prepared and submitted to the action of hydrolysing and reducing agents. The compounds are very different from the ω-bromoxylenes and very similar to one another in chemical and physical properties. They are quite stable towards aqueous alcohol at 76° and towards an aqueous acetic acid solution of hydrogen iodide. Differences in the rate of hydrolysis by aqueous-alcoholic sodium hydroxide have been observed and the order is: unsubs. (1·25) > *m*(0·83) > *p*(0·7) > *o*(0·6), but the differences are exceedingly small. (The figures in brackets denote the reciprocal of the time taken for half hydrolysis of the bromide at 76°, *i.e.*, an approximate rate of hydrolysis; compare Shoesmith and Slater, J., 1926, 214.) There appears to be a very slight residuum of alternating effect, and all the substituted compounds are slightly more difficult to hydrolyse than β-phenylethyl bromide—the reverse of the case in the corresponding benzyl bromides.

The *o*-isomeride is the most difficultly hydrolysable. The anomalous position of *o*-isomerides has been repeatedly stressed (as has also the fact that this is not due to steric influences; Shoesmith and Slater, J., 1926, 215). Olivier has arrived independently at the same conclusion (*Rec. trav. chim.*, 1926, **45**, 452, 710). As yet no satisfactory explanation has been given of the factors governing the reactivity of ortho-substituted benzyl bromides, save that there is here present an influence which renders them less reactive to hydrolysing and more reactive to reducing agents (*e.g.*, hydrogen iodide) than would be expected from any of the various theories put forward to explain enhanced and subdued reactivity.

It may now with certainty be concluded that those influences the effect of which was demonstrated so clearly in the isomeric ω-bromoxylenes are only feebly transmitted through the α-carbon atom of the side chain in the β-tolylethyl bromides, a conclusion of special interest in view of recent observations (Ing and Robinson, J., 1926, 1656; Goss, Hanhart, and Ingold, this vol., p. 250) that a very appreciable general effect due to positively charged nitrogen

is transmitted through two singly bound carbon atoms directly attached to the benzene nucleus.

EXPERIMENTAL.

The isomeric β-tolylethyl bromides were prepared according to the general scheme:

$$CH_3\cdot C_6H_4Br \xrightarrow{Mg} CH_3\cdot C_6H_4\cdot MgBr \xrightarrow{CH_2Cl\cdot CH_2\cdot OH}$$
$$CH_3\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot OH \xrightarrow{PBr_3} CH_3\cdot C_6H_4\cdot CH_2\cdot CH_2Br.$$

The Isomeric β-Tolylethyl Alcohols.—Grignard's method (*Compt. rend.*, 1905, **141**, 44) was modified in several important particulars. To the bromotoluene (64 g., carefully freed from traces of possible phenolic impurities) in 250 c.c. of dry ether, 9 g. of magnesium were added and, when the vigorous reaction ended, dry, freshly distilled ethylene chlorohydrin (10 g.), dissolved in an equal volume of dry ether, was slowly dropped in. After the vigorous reaction had abated, the ether was distilled away and the residue was heated under 14 mm. pressure at a temperature not exceeding 180—200° for 2 hours to remove toluene, ditolyl, etc.; it was then mixed with ice and after 30 minutes the decomposition was completed by the addition of the calculated quantity of sulphuric acid in ice-water. The ethereal extract of this solution was dried, the ether distilled away, and the residue heated for about 10 minutes with aqueous-alcoholic potash. Extraction with ether, drying, and distillation, finally in a vacuum, then gave the β-tolylethyl alcohol in 20—24% yield, and no improvement could be effected. The alcohols had b. p.'s: *o*-isomeride, 115—116°/13 mm. (compare Grignard, *loc. cit.*); *m*-isomeride, 115—117°/13 mm. (Braun, Grabowski, and Kirschbaum, *Ber.*, 1913, **46**, 1266); and *p*-isomeride, 116·5—118°/14 mm. (Grignard).

The Isomeric β-Tolylethyl Bromides.—As hydrogen bromide has no effect on these alcohols, the bromides were prepared by adding phosphorus pentabromide (60 g.) to 15 g. of the respective β-tolylethyl alcohols, dissolved in 50 c.c. of dry benzene, the reaction being controlled by shaking in ice-water and completed by heating for 1 hour at a temperature not exceeding 50°. The mixture was then poured on excess of ice, and the bromide was extracted with ether, dried over sodium sulphate, and distilled in a vacuum. The distillate was washed with water to remove final traces of phosphoryl bromide, dried, and redistilled. The bromides all boiled, as expected, at a lower temperature than the corresponding alcohols. They had b. p.'s: *o*-compound, 99—100°/10 mm.; *m*-compound, 101—103°/11 mm.; and *p*-compound, 103·5—105°/11 mm. They con-

tained hydrolysable bromine: *o*-isomeride, 39·4; *m*-isomeride, 39·8; and *p*-isomeride, 40·3% ($C_9H_{11}Br$ requires hydrolysable Br, 40·2%). They are stable, sweet-smelling, non-pungent, non-lachrymatory oils, thus differing sharply from the corresponding ω-bromoxylenes.

β-Phenylethyl bromide was prepared from freshly distilled, commercial β-phenylethyl alcohol in a similar manner and, for comparative purposes, to make quite sure that only the *ethyl* bromides are formed by the action of phosphorus pentabromide on the alcohols, a sample was prepared by a method suggested to us by Professor Lapworth. A mixture of β-phenylethyl alcohol (20 g.) and constant-boiling hydrobromic acid (50 c.c.) was boiled under reflux for 4 hours. The bromide so formed was washed with water until free from halogen acid, dried, and distilled. The samples obtained by the two methods had identical boiling points, 89—89·5°/12 mm., estimations of hydrolysable bromine showed they were pure, and later the rate of hydrolysis showed they were identical.

Behaviour towards Hydrogen Iodide.—All the bromides were stable to hydrogen iodide in aqueous acetic acid at 100° for 4 hours. For comparative purposes, some unpublished observations, made in collaboration with Dr. R. H. Slater, on ω-bromo-*m*- and -*p*-xylenes are given in order to stress the differences observed in the two cases. These figures were obtained in a similar manner, but at 110° (experience has shown that slightly different results are obtained at the two temperatures); t, w, and x have the usual significance.

TABLE I.

	ω-Bromo-*m*-xylene.		ω-Bromo-*p*-xylene.*	
t (hrs.).	w.	x.	w.	x.
1	0·1239	69	0·1208	44
2	0·1245	87	0·1217	66
3	0·1225	100	0·1286	75

* The *p*-isomeride is not reduced by hydrogen iodide in glacial acetic acid at 25°. Its reduction at 110° shows the powerful reducing action of the aqueous acetic acid reagent at this temperature.

Hydrolysis of the Isomeric β-Tolylethyl Bromides.—The bromides were stable to aqueous alcohol at 76° for 4 hours. Comparative hydrolysis figures were obtained as follows: The bromide (approx. 0·50 g.) was dissolved in 75 c.c. of absolute alcohol, 25 c.c. of N/10-sodium hydroxide were added, and the volume was made up to 103 c.c. Aliquot portions (20 c.c.) were heated in a thermostat at 76° (b. p. of carbon tetrachloride) for definite times, and the amount

of hydrolysis which had taken place was estimated by titrating the unused alkali with standard hydrochloric acid. The results are in Table II.

TABLE II.

	o-Isomeride. $w = 0{\cdot}501$.	*m*-Isomeride. 0·506.	*p*-Isomeride. 0·500.	β-Phenylethyl bromide. 0·453.
t (hrs.).	*x*.	*x*.	*x*.	*x*.
½	38	45	46	56
1	54	63	56	68
2	69	75	71	81
4	82	86	83	89
6	85	90	87	93

The order of reactivity with *N*/30-alcoholic potassium hydroxide at 25° was exactly the same.

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EDINBURGH UNIVERSITY. [*Received, May 4th*, 1927.]

CCXXXII.—*Reduction of Silver Compounds in Alkaline Solution.*

By WALTER FARMER and JAMES BRIERLEY FIRTH.

THE object of the present investigation was to ascertain the conditions of experiment leading to the production of a maximum yield of metallic silver when ammoniacal solutions of certain silver compounds are reduced in the presence of aluminium and aqueous caustic alkali.

The reduction of silver oxide, prepared from silver nitrate, may be simply represented by the equations

(i) $6AgNO_3 + 6KOH = 3Ag_2O + 6KNO_3 + 3H_2O$,
(ii) $2Al + 6KOH = 2Al(OK)_3 + 3H_2$,
(iii) $3Ag_2O + 3H_2 = 6Ag + 3H_2O$,

one g.-atom of aluminium being equivalent to 3 g.-atoms of silver.

Preliminary experiments indicated that, in the absence of aluminium, heating of ammoniacal silver solutions in the presence of potassium hydroxide was followed by detonation. Addition of potassium hydroxide to concentrated solutions of silver compounds in aqueous ammonia caused the formation of black pre-

cipitates. Hydrolysis in the presence of traces of aluminium led to the detonation of such reaction mixtures. Hydrolysis of the dried black precipitates by potassium hydroxide gave silver oxide as the final product. In the presence of ammonia, spongy silver was formed. Analysis of the dried black precipitates by the Kjeldahl method showed that they were mixtures of silver nitride with relatively small quantities of silver oxide.

Experimental.

Series I.—An ammoniacal solution of silver nitrate containing 2 g. of the salt, 25 c.c. of ammonia (*d* 0·880), and 25 c.c. of water was treated with 25 c.c. of 3*N*-potassium hydroxide, and heated at 100° in a water-bath. At once a black film began to form on the walls of the reaction vessel, and its appearance was followed by an explosion which shattered the reaction vessel. This phenomenon occurred in three consecutive experiments, detonation taking place after a lapse of 12, 14, and 15 minutes from the commencement of the reaction.

Series II.—Aqueous silver nitrate solutions of various concentrations were treated with just sufficient ammonia (*d* 0·880) to redissolve the precipitated silver oxide, and to each solution were added 10 g. of potassium hydroxide dissolved in 15 c.c. of water. A brown precipitate formed; this was followed by a black precipitate as more caustic alkali was added. The final heavy precipitate was uniformly black in colour. The reaction vessel was then placed in a water-bath and heated to 100°. The black precipitate was thereby progressively reduced to a grey, metallic powder. The reduced metal was filtered, washed, dried, and analysed. In all cases, the filtrates were free from silver. Under the conditions of these experiments, it was observed that quantities of silver nitrate not exceeding 5 g. could be quantitatively reduced to metal. Attempts to reduce the silver salt in larger quantities invariably led to the explosion of the product. Typical results are given in Table I.

Table I.

Wt. of $AgNO_3$ (g.).....	0·5	1·0	2·0	3·0	4·0	5·0
% Ag ppd.	99·82	99·85	99·91	99·83	99·87	99·89
% Ag in ppt.	99·61	99·70	99·82	99·80	99·84	99·85

The conversion of the black precipitate into metallic silver was associated with the evolution of a gas, which was found to be nitrogen. The results of a quantitative examination of this reaction are summarised in the first two lines of Table II, and the last two

lines show that the nitrogen evolved is chemically equivalent to the silver nitrate used. A similar result was obtained with silver chloride.

TABLE II.

Wt. of $AgNO_3$ (g.)	0·1619	0·2269	0·3176	0·4055	0·5892
Nitrogen (c.c. at *N.T.P.*)...	3·41	4·86	6·72	8·62	12·41
$AgNO_3$ (mg.-equiv.)	0·95	1·33	1·87	2·37	3·47
$\frac{1}{3}N$ (mg.-equiv.)	0·91	1·30	1·80	2·31	3·33

Series III.—Several samples of the black product were prepared as in Series II, 0·5 g. of silver nitrate being used in each case. Ordinary test-tubes were used as reaction vessels. One fragment of aluminium filings was quickly dropped into each reaction mixture, and the tubes were immediately immersed in vessels containing water at known temperatures. The observations were as follows :

(*a*) At 50°, crackling sound; (*b*) 60°, report; tube intact; (*c*) 70°, report, but louder; tube intact; (*d*) 90°, explosion; tube shattered; (*e*) 100°, violent explosion; tube shattered.

Analysis of the Black Precipitate.—A quantity of the black precipitate was prepared as in Series II. After 15 minutes, the supernatant liquor was decanted off, and the precipitate was washed by decantation with water and transferred to a filter. After thorough washing with water, the black precipitate was washed into a small tared evaporating dish, the excess of water evaporated on the water-bath, and the final drying completed by preserving over concentrated sulphuric acid. The product, which did not smell of ammonia, was then analysed. Owing to the great instability of the product, which exploded on percussion and even on touching with a spatula, it was deemed advisable to analyse it in bulk according to the following scheme :

(*a*) The black product was hydrolysed by means of strong caustic alkali, and the evolved ammonia estimated by absorption in standard sulphuric acid.

(*b*) The residual silver oxide was washed, dried, weighed, converted into nitrate, precipitated as chloride, and weighed in this form.

(*c*) The alkaline filtrate, from which the black product had been isolated, was examined for dissolved silver, which was precipitated and weighed as chloride. A typical result is given in Table III.

TABLE III.

Wt. of black ppt.	= 1·133 g.	$AgNO_3$ precipitated	= 85·13%
Nitrogen in ppt.	= 3·59%	$AgNO_3$ remaining in solution	= 15·03%
Ag in ppt.	= 95·48%		

From the above result, it would appear that the product was not homogeneous. In order to test this view the final, dry, black precipitate, prepared as above, was extracted several times with 50 c.c. of 10% ammonia solution. Analysis of the product after extraction and of the ammoniacal extract gave the following result.

TABLE IV.

Wt. of ppt. before extraction	= 1·132 g.	% of total $AgNO_3$ ppd.	= 84·68
Wt. of ppt. after extraction	= 0·989 g.	% of $AgNO_3$ in extract	= 10·33
Nitrogen in ppt.	= 4·11%	% of $AgNO_3$ in solution	= 15·19
Silver in ppt.	= 95·50%		

From a series of experiments, it was ascertained that a similar black precipitate containing nitrogen could be obtained when silver chloride was used instead of silver nitrate.

Series IV.—Reduction at 100°, *in ammoniacal solution, using varying quantities of aluminium and definite amounts of dissolved silver in the presence of potassium hydroxide.* The required quantity of the silver compound, containing silver equivalent to that present in 2 g. of the nitrate, was treated in an ammoniacal solution, containing 25 c.c. of ammonia (*d* 0·880) and 25 c.c. of water, with 25 c.c. of 3*N*-potassium hydroxide. A definite quantity of aluminium filings was then added and the reduction carried out at 100°; a black product was deposited, the colour of which changed rapidly to grey; from this stage onwards the quantity of the reduced metal increased continuously throughout the experiment. The final product formed grey, coherent masses of reduced silver possessing a vesicular structure. The reduction was complete in 1½ hours, and the reaction liquid was then treated with 10 c.c. of ammonia (*d* 0·880), allowed to stand for 15 minutes with frequent shaking, diluted with half its bulk of distilled water, and filtered through a tared Gooch crucible. The reduced silver was thoroughly washed, dried at 100°, weighed, and analysed. The results for silver nitrate are given in Table V, and those for silver oxide and silver chloride were very similar.

TABLE V.

Al used (g.)	0·05	0·10	0·20
Ag ppd., %	99·88	99·82	99·79
Ag in ppt., %	99·83	99·89	99·87

Series V.—A solution was prepared exactly as in Series IV, a strip of sheet aluminium was placed in it, and, immediately, a black deposit formed on the surface of the metal. After 30 seconds, the strip was removed, the deposit transferred to a beaker by means of a jet of water, and the strip reimmersed in the silver solution. This was repeated (10 times) until the deposit had been

obtained in a quantity sufficient for analysis, which showed it to be elementary silver.

Series VI.—Ammoniacal solutions of silver nitrate were prepared, the ammonia content being just sufficient to retain the silver in solution. 2 C.c. of ammonia (*d* 0·880) were added, *i.e.*, excess sufficient to prevent the formation of black precipitates (total maximum bulk, 10 c.c.). Each solution was treated with 2 g. of potassium hydroxide dissolved in 5 c.c. of water, the required quantity of aluminium added, and the dissolved silver submitted to reduction at 100°. The volume of gas evolved was determined, and the gas proved to be nitrogen. Typical results are given in Table VI.

TABLE VI.

Wt. of Al (g.)	0·01	0·01	0·01	0·02	0·03
Wt. of $AgNO_3$ (g.)	0·2884	0·5378	0·7500	0·7500	0·7500
Nitrogen (c.c. at *N.T.P.*)	1·92	7·33	11·97	7·89	3·78
% Ag ppd.	99·52	99·81	99·82	99·88	99·84

It was observed that the evolution of nitrogen was retarded.

The results obtained indicate that the amount of silver reduced is stoicheiometrically equal to the aluminium dissolved *plus* the nitrogen evolved, *i.e.*, that Ag^+ reduced = Al oxidised + NH_3 oxidised, thus (in mg.-equivs.) :

$\frac{1}{3}$Al	1·1	1·1	1·1	2·2	3·3
$\frac{1}{3}$N	0·5	2·0	3·2	2·1	1·0
Sum	1·6	3·1	4·3	4·3	4·3
$AgNO_3$	1·7	3·2	4·4	4·4	4·4

Series VII.—Reduction at 100°, *in ammoniacal solution, using a fixed quantity of aluminium, and varying amounts of dissolved silver in the presence of potassium hydroxide.* The object of this series was to ascertain the maximum effect of a definite quantity of aluminium under given conditions of experiment. 0·05 G. of aluminium was used in each case. The bulk of the mixed solutions and the concentration of ammonia were similar to those of Series IV. The quantities of silver compound used were equivalent to 2—8 g. of nitrate. In all experiments up to a silver content equivalent to 6 g. of nitrate, a quantitative yield of silver was obtained. The use of more concentrated solutions of silver frequently resulted in explosions. In this series it was observed that the first-formed, coherent masses of silver gradually changed to a granular powder. The results are given in Table VII.

TABLE VII.

Wt. of Ag compd. (g.) ...	2	3	4	5	6
Wt. of Ag ppd. (g.)	1·27	1·90	2·54	3·17	3·80
% Ag ppd.	99·73	99·82	99·79	99·83	99·89
% Ag in ppt.	99·79	99·88	99·85	99·80	99·84

Series VIII.—Reduction at 100°, *in ammoniacal solution, using definite quantities of aluminium in the presence of potassium hydroxide, the solutions of silver used during the process of reduction being added from time to time in measured volumes of known ammonia and silver content.* From the preceding series it seemed probable that the concentration of the silver salt relative to the ammonia content of the alkaline solution employed is a factor governing the stability of the ammoniacal solutions submitted to reduction. The present series was carried out to test this view.

A solution containing 2 g. of silver salt, prepared as in Series IV, was treated with 0·05 g. of aluminium filings. An additional series of solutions was prepared containing 2 g. of the same silver salt in 25 c.c. of ammonia (*d* 0·880) and 25 c.c. of water. At the end of consecutive intervals of 20 minutes, these solutions were, in turn, added to the reaction liquid undergoing reduction. The total quantity of silver salt thus added was equivalent to 8 g. of the silver salt employed. The resulting reduced silver formed grey, coherent masses. The results are given in Table VIII.

TABLE VIII.

	From $AgNO_3$.	From AgCl.
Wt. of ppt. (g.)	4·26	3·64
% Ag in ppt.	99·89	99·85
% Ag ppd.	66·94	48·27

Series IX.—As in Series VIII, activated silver being used instead of aluminium filings. Quantities of reduced silver, prepared as in Series IV, were activated by heating in a vacuum in a quartz tube for 3 hours at 900°, the samples of the metal obtained from the different salts being submitted to heat treatment separately. The method of experiment was as in Series VIII. The total quantity of silver salt added was equivalent to 8 g. of the silver salt used. Two series of experiments were carried out on activated silver from (i) silver nitrate, and (ii) cf. silver chloride. Table IX contains the results for the first series.

TABLE IX.

Activated Ag used (g.).	$AgNO_3$.			AgCl.		
	Wt. of ppt. (g.).	% Ag in ppt.	% Ag ppd.	Wt. of ppt. (g.).	% Ag in ppt.	% Ag ppd.
0·4	2·54	99·89	39·91	1·96	99·87	26·05
0·6	3·11	99·92	48·89	2·73	99·90	36·29
0·8	3·61	99·87	56·80	2·81	99·88	37·42
1·0	3·95	99·84	62·15	3·08	99·85	40·82

Discussion and Conclusions.

Under the conditions of experiment for hydrolysis at 100°, the black precipitates are transformed to metallic silver, while the

reaction liquids are found to be free from dissolved silver. In so far as the black precipitates are unstable in the presence of traces of aluminium, it would seem that deposition of silver nitride, prior to the final separation of metallic silver, is entirely inhibited with respect to the different processes of reduction which proceed without detonation of the reaction mixture.

In the absence of aluminium, the different amounts of dissolved silver quantitatively separated as reduced metal are equivalent to the volumes of nitrogen evolved. In the presence of aluminium, the evolution of nitrogen is inhibited : the formation of this gas does not commence until every trace of metallic aluminium has been dissolved as aluminate.

The quantitative yields of reduced silver obtained under conditions for the production of nitrogen in presence of aluminium would appear, therefore, to be the cumulative effect of two distinct reactions. In the first reaction, metallic silver is separated from the solution in a quantity equivalent to the amount of aluminium employed. The newly deposited silver, being in a finely divided condition, serves to stabilise the ammoniacal solution containing the remainder of the silver present in the dissolved state, and, as in the experiments involving the employment of activated silver (compare Series IX), it imparts to the silver solution the increment of energy necessary for the commencement of the second reaction. The second reaction then proceeds to completion, the deposition of silver being accompanied by the evolution of nitrogen in the proportion of 3 atoms of silver to 1 atom of nitrogen.

It would seem, therefore, that, in the presence of ammonia, caustic alkali effects precipitation of silver nitride, with small amounts of silver oxide, through the formation of an intermediate complex, $(NH_3)_2AgOH$, according to the following equations :

$$\text{(Ai)}\quad (NH_3)_2AgNO_3 + KOH = (NH_3)_2AgOH + KNO_3,$$
$$\text{(Aii)}\quad (NH_3)_2AgCl + KOH = (NH_3)_2AgOH + KCl,$$
$$\text{(B)}\quad 3(NH_3)_2AgOH + 2H_2O = 5NH_4OH + NAg_3,$$
$$\text{(C)}\quad 2(NH_3)_2AgOH + 3H_2O = 4NH_4OH + Ag_2O$$

(compare Bodländer and Fittig, *Z. physikal. Chem.*, 1902, **39**, 597; Straub, *ibid.*, 1911, **77**, 331).

At 100° the reactions represented by (B) and (C) are suppressed, decomposition of the diamminoargentic complex, evolution of nitrogen, and separation of silver taking place according to the equation

$$\text{(D)}\quad 6(NH_3)_2AgOH + 4H_2O = 6Ag + N_2 + 10NH_4OH.$$

It is concluded that the first reaction takes place, in the presence of aluminium, accompanied by changes conveniently represented

by the equations given on p. 1772. The second reaction involves transformations represented by the equations (Ai or Aii), (B), (C), and (D).

The results of Series IV and VII show that the extent of reduction is determined by the conditions of experiment. Thus, in Series VII, 6 g. of silver nitrate in 75 c.c. of reaction solution are completely reduced by the introduction of 0·05 g. of aluminium. By the modifications introduced in Series VIII larger quantities can be reduced without explosion, and 0·05 g. of aluminium reduces 6·694 g. of silver nitrate or 4·827 g. of silver chloride.

Series IX shows that, in absence of aluminium, ammoniacal solutions of silver nitrate or silver chloride may be reduced by means of freshly reduced silver from Series IV, activated by heating in a vacuum for 3 hours at 900°, 1 g. of activated silver being capable of reducing 6·215 g. or 4·082 g. of silver nitrate or chloride, respectively.

The continuous separation of finely divided silver in the form of grey, coherent masses possessing a vesicular structure is constantly exposing an ever-increasing surface of metal to the ammoniacal solution undergoing reduction. Uninterrupted contact between the surface of the newly deposited metal and the solution induces energy changes involving decay in the activity of the reduced metal followed by the separation of further quantities of silver from the solution. Prolonged contact between the reduced metal and the solution ultimately brings about a marked decay in the activity of the reduced metal, and this change is accompanied by the following characteristic effects. The coherent masses of reduced metal gradually break down to a powder, whilst the continued isolation of silver from the solution is ultimately brought to a limit beyond which no further appreciable deposition of reduced metal takes place.

In the presence of relatively large amounts of ammonia, separation of silver from ammoniacal silver solutions can be effected only when a suitable source of energy is introduced into the reacting system. Under given conditions of experiment, aluminium, in the presence of aqueous caustic alkali, may be employed to induce and control the production of reduced silver. When the ammoniacal concentration of the solution undergoing reduction has fallen to a certain limiting value, the concentration of the dissolved silver rises to a value such that it is unnecessary to supply energy to the reacting system: the residual ammonia is then unable to control the reaction, whilst the external heat applied in order to maintain the temperature of the reaction becomes more than sufficient to supply the energy necessary to allow the reaction to continue, with

reaction liquids are found to be free from dissolved silver. In so far as the black precipitates are unstable in the presence of traces of aluminium, it would seem that deposition of silver nitride, prior to the final separation of metallic silver, is entirely inhibited with respect to the different processes of reduction which proceed without detonation of the reaction mixture.

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$$\text{(B)}\quad 3(NH_3)_2AgOH + 2H_2O = 5NH_4OH + NAg_3,$$
$$\text{(C)}\quad 2(NH_3)_2AgOH + 3H_2O = 4NH_4OH + Ag_2O$$

(compare Bodländer and Fittig, *Z. physikal. Chem.*, 1902, **39**, 597 ; Straub, *ibid.*, 1911, **77**, 331).

At 100° the reactions represented by (B) and (C) are suppressed, decomposition of the diamminoargentic complex, evolution of nitrogen, and separation of silver taking place according to the equation

$$\text{(D)}\quad 6(NH_3)_2AgOH + 4H_2O = 6Ag + N_2 + 10NH_4OH.$$

It is concluded that the first reaction takes place, in the presence of aluminium, accompanied by changes conveniently represented

by the equations given on p. 1772. The second reaction involves transformations represented by the equations (Ai or Aii), (B), (C), and (D).

The results of Series IV and VII show that the extent of reduction is determined by the conditions of experiment. Thus, in Series VII, 6 g. of silver nitrate in 75 c.c. of reaction solution are completely reduced by the introduction of 0·05 g. of aluminium. By the modifications introduced in Series VIII larger quantities can be reduced without explosion, and 0·05 g. of aluminium reduces 6·694 g. of silver nitrate or 4·827 g. of silver chloride.

Series IX shows that, in absence of aluminium, ammoniacal solutions of silver nitrate or silver chloride may be reduced by means of freshly reduced silver from Series IV, activated by heating in a vacuum for 3 hours at 900°, 1 g. of activated silver being capable of reducing 6·215 g. or 4·082 g. of silver nitrate or chloride, respectively.

The continuous separation of finely divided silver in the form of grey, coherent masses possessing a vesicular structure is constantly exposing an ever-increasing surface of metal to the ammoniacal solution undergoing reduction. Uninterrupted contact between the surface of the newly deposited metal and the solution induces energy changes involving decay in the activity of the reduced metal followed by the separation of further quantities of silver from the solution. Prolonged contact between the reduced metal and the solution ultimately brings about a marked decay in the activity of the reduced metal, and this change is accompanied by the following characteristic effects. The coherent masses of reduced metal gradually break down to a powder, whilst the continued isolation of silver from the solution is ultimately brought to a limit beyond which no further appreciable deposition of reduced metal takes place.

In the presence of relatively large amounts of ammonia, separation of silver from ammoniacal silver solutions can be effected only when a suitable source of energy is introduced into the reacting system. Under given conditions of experiment, aluminium, in the presence of aqueous caustic alkali, may be employed to induce and control the production of reduced silver. When the ammoniacal concentration of the solution undergoing reduction has fallen to a certain limiting value, the concentration of the dissolved silver rises to a value such that it is unnecessary to supply energy to the reacting system: the residual ammonia is then unable to control the reaction, whilst the external heat applied in order to maintain the temperature of the reaction becomes more than sufficient to supply the energy necessary to allow the reaction to continue, with

the result that the reaction is accelerated, and ultimately proceeds with explosive velocity. In these circumstances, therefore, the employment of aluminium, in the presence of caustic alkali, is quite unnecessary, and can lead only to an increase in the intensity of the explosive effects observed (compare Baly, *Ann. Report*, 1921, **18**, 40).

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, April 8th*, 1927.]

CCXXXIII.—*Molecular Volumes at Absolute Zero. Part I. Density as a Function of Temperature.*

By SAMUEL SUGDEN.

DURING the last few years it has been shown by the author and others that there are several empirical relations between surface tension, density, and temperature which hold with considerable accuracy over a large range of the variables concerned. Of these, the most important for the present discussion are van der Waals's equation (*Z. physikal. Chem.*, 1894, **13**, 716) for the variation of surface tension with temperature,

$$\gamma = \gamma_0(1 - T_r)^{6/5} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and Macleod's relation (*Trans. Faraday Soc.*, 1923, **19**, 38) between surface tension and density,

$$\gamma = C(D - d)^4 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In these equations, γ is the surface tension, T_r the reduced temperature, D and d are the densities of the liquid and saturated vapour, respectively, and γ_0 and C are constants.

The first equation has been shown to give the experimental values of the surface tension of non-associated liquids from the ordinary temperature to within a few degrees of the critical point (Sugden, J., 1924, **125**, 32). Equation (2) was shown by the present author to hold for a large number of liquids over a wide range of temperatures. Further, from this equation is derived the formula for calculating the parachor $[P]$ where

$$[P] = MC^{1/4} = M\gamma^{1/4}/(D - d) \quad . \quad . \quad . \quad . \quad (3)$$

(M = molecular weight). This constant is found to be an accurately additive function of certain atomic and structural constants (Sugden, J., 1924, **125**, 1177; Sugden, Reed, and Wilkins, J., 1925, **127**, 1525; Sugden and Whittaker, *ibid.*, p. 1868; Sugden and Wilkins,

ibid., p. 2517; this vol., p. 139), and in particular provides a clear experimental distinction between non-polar and semipolar double bonds.

These two equations, although empirical and at present not related to any theory of the liquid state, are supported by a considerable amount of experimental evidence. From them, it is obviously possible to deduce a number of other relationships between the variables concerned, including a modified form of the Ramsay-Shields equation (compare Ferguson, *Trans. Faraday Soc.*, 1923, **19**, 41, 407). The simplest of these is a relation between density and temperature

$$D - d = D_0(1 - T_r)^{3/10} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which is obtained by eliminating γ between equations (1) and (2). Abundant material for testing this equation is to be found in the data of Young (*Proc. Roy. Soc. Dublin*, 1910, **12**, 374), which include measurements of the liquid and vapour densities of 30 substances. For all of them equation (4) is found to hold with remarkable accuracy; to save space, however, the calculations will only be given for the liquids to which equation (1) has been applied in a previous communication.

Equation (4) contains two constants, D_0 and the critical temperature, since $T_r = T/T_c$. These were determined by calculating the value of $(D - d)^{10/3}$ at intervals of 40°, since this quantity is a linear function of temperature, and applying the method of "zero sum" (Campbell, *Phil. Mag.*, 1920, **39**, 177; 1924, **47**, 816). The constants obtained in this manner were then used to calculate the density difference $(D - d)$ at each temperature; the results are shown in Table I, from which it will be seen that equation (4) reproduces the experimental data with a high degree of accuracy—in general the difference between the observed and the calculated values of $D - d$ is 1 part in 500 parts. A few greater deviations are found in the neighbourhood of the critical point, but in this region it is difficult to measure the density of the saturated vapour with precision.

The six liquids named in Table I belong to the class of unassociated liquids. Table II gives similar data for two associated liquids, *viz.*, acetic acid and ethyl alcohol, and shows that equation (4) holds for a part of the range; above a definite temperature, however, the density decreases more rapidly than is indicated by the formula, and the critical point is reached at a lower temperature than would be expected from the slope of the density–temperature curve at low temperatures. This effect is scarcely appreciable for acetic acid, but more pronounced for ethyl alcohol. It would seem, therefore, that association has little or no influence on the density, provided

Table I.

Variation of Density with Temperature.

	Benzene.			Chlorobenzene.		
t.	$D-d$ (obs.).	$D-d$ (calc.).	Diff.	$D-d$ (obs.).	$D-d$ (calc.).	Diff.
0°	0·9000	0·8968	−0·0032	1·1279	1·1237	−0·0042
40	0·8568	0·8571	+0·0003	1·0844	1·0845	+0·0001
80	0·8118	0·8126	+0·0008	1·0411	1·0420	+0·0009
120	0·7615	0·7615	±0·0000	0·9934	0·9944	+0·0010
160	0·7012	0·7008	−0·0004	0·9412	0·9416	+0·0004
200	0·6250	0·6246	−0·0004	0·8804	0·8795	−0·0009
240	0·5137	0·5169	+0·0032	0·8056	0·8057	+0·0001
280	0·2854	0·2743	−0·0111	0·7342	0·7378	+0·0036 (270°)
	t_c (obs.), 288·5.			t_c (obs.), 359·2.		
	Ethyl ether.			Methyl formate.		
0°	0·7354	0·7368	+0·0014	1·0025	1·0030	+0·0005
40	0·6857	0·6866	+0·0009	0·9415	0·9416	+0·0001
80	0·6286	0·6260	−0·0026	0·8698	0·8692	−0·0006
120	0·5471	0·5475	+0·0004	0·7801	0·7793	−0·0008
160	0·4256	0·4270	+0·0014	0·6513	0·6550	+0·0037
180	0·3133	0·3129	−0·0004	0·4134	0·4134	±0·0000 (200°)
	t_c (obs.), 193·8.			t_c (obs.), 214.		
	Ethyl acetate.			Carbon tetrachloride.		
0°	0·9243	0·9235	−0·0008	1·6323	1·6301	−0·0022
40	0·8754	0·8760	+0·0006	1·5540	1·5558	+0·0018
80	0·8210	0·8217	+0·0007	1·4704	1·4722	+0·0018
120	0·7580	0·7571	−0·0009	1·3738	1·3758	+0·0020
160	0·6775	0·6767	−0·0008	1·2617	1·2605	−0·0012
200	0·5630	0·5641	+0·0011	1·1146	1·1134	−0·0012
240	0·3279	0·3296	+0·0017	0·8980	0·8973	−0·0007
	t_c (obs.), 250·1.			t_c (obs.), 283·15.		

that the degree of association does not change with temperature. This conclusion is supported by the fact that the value of D_0 found for acetic acid is almost identical with that for its isomeride methyl formate, whilst the values for the alcohols, as will be shown in the following paper, are those to be expected from their composition.

Table II.

Variation of Density with Temperature. (Associated liquids.)

	Acetic acid.			Ethyl alcohol.		
t.	$D-d$ (obs.).	$D-d$ (calc.).	Diff.	$D-d$ (obs.).	$D-d$ (calc.).	Diff.
0°	1·0697	1·0700	+0·0003	0·8065	0·8070	+0·0005
40	1·0282	1·0288	+0·0006	0·7719	0·7720	+0·0001
80	0·9825	0·9826	+0·0001	0·7331	0·7326	−0·0005
120	0·9329	0·9315	−0·0014	0·6859	0·6876	+0·0017
160	0·8740	0·8722	−0·0018	0·6137	0·6344	+0·0207
200	0·8060	0·8020	−0·0040	0·5060	0·5682	+0·0522
240	0·7138	0·7136	−0·0002	0·2110	0·4764	+0·2654
280	0·5746	0·5878	+0·0132	—	—	—
	t_c (obs.), 321·6.			t_c (obs.), 243·1.		

The critical temperatures predicted from the density observations are collected in Table III and are compared with the observed values and also with the values deduced from the variation of surface tension with density (Sugden, J., 1924, **125**, 32). It will be seen that, in general, the unassociated liquids give a good agreement between the observed and the calculated critical temperatures, whilst for associated liquids the observed critical temperature is markedly lower than that predicted from the lower part of the density curve.

TABLE III.

	Critical temperature		
Substance.	from density.	from surface tension.	obs.
Benzene	285·5°	287°	288·5°
Chlorobenzene	358	358	359·2
Ethyl ether	191	193	193·8
Methyl formate	211	212	214
Ethyl acetate	248	249	250·1
Carbon tetrachloride	278	280	283·1
Methyl alcohol	279	—	240
Ethyl alcohol	290	—	243·1
Acetic acid	324	—	321·6

Since equation (4) represents the variation of density with temperature with great precision as the temperature increases, it is reasonable to suppose that it will also hold as the temperature decreases. The constant D_0 is therefore of considerable interest, since it represents the density of the supercooled liquid at absolute zero. The values of this constant are collected in Table IV, and if

TABLE IV.

Zero Volumes and the Parachor.

Substance.	D_0.	V_0.	$[P]$.	$[P]/V_0$.
Benzene	1·0965	71·2	207·1	2·91
Chlorobenzene	1·3323	84·4	244·3	2·89
Ethyl ether	0·9616	77·1	210·0	2·73
Methyl formate	1·2863	46·7	138·0	2·96
Ethyl acetate	1·1538	76·4	216·0	2·83
Carbon tetrachloride	2·0015	77·4	222·0	2·87
Methyl alcohol	0·9936	32·3	93·2*	2·89
Ethyl alcohol	0·9846	46·8	132·2*	2·82
Acetic acid	1·2853	46·7	138·0*	2·96

* Calculated from the atomic and structural constants.

these numbers are divided into the molecular weight of the liquid, the molecular volume (V_0) at absolute zero is obtained: this will be referred to as the "zero volume." The column headed $[P]$ gives the calculated value of the parachor for each liquid, and the fifth column shows that the ratio $[P]/V_0$ is nearly constant for the nine

substances tabulated. This constancy must, however, be regarded as fortuitous, since from equations 1, 3, and 4 it is readily shown that

$$[P] = \gamma_0^{1/4} V_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

For organic substances γ_0 has values ranging from about 60 to 80, so the fourth root of this, which gives the ratio $[P]/V_0$, does not vary much. If, however, the range is extended on the one hand to hydrogen, which has a small value of γ_0, and on the other hand to metals and their salts, which have large surface tensions, it is found that the zero volume is no longer proportional to the parachor.

A relation of greater significance is exhibited in Table V, which shows that the zero volume is very nearly a constant fraction of the critical volume. The data for hydrogen are given by Onnes (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 528), and those for the other substances by Young (*loc. cit.*). Except in the case of hydrogen the ratio V_0/V_c is very nearly constant over the whole range considered.

TABLE V.

Zero Volumes and Critical Volumes.

Substance.	V_0.	V_c.	V_0/V_c.
Hydrogen	22·0	46·9	0·373
Ethyl ether	77·1	281·9	0·273
Carbon tetrachloride	77·4	276·1	0·280
Methyl formate	46·7	172·0	0·271
Methyl acetate	61·1	227·8	0·268
Methyl propionate	75·5	282·0	0·268
Ethyl acetate	76·4	286·3	0·267
Propyl formate	76·7	284·8	0·269
Methyl butyrate	90·7	340·1	0·267
Methyl *iso*butyrate	90·6	335·9	0·267
Ethyl propionate	90·9	344·3	0·264
Propyl acetate	91·3	345·3	0·264
n-Pentane	83·9	310·3	0·270
*iso*Pentane	86·1	307·0	0·280
Di*iso*propyl	99·9	357·3	0·280
n-Heptane	114·9	427·1	0·269
n-Octane	130·8	490·7	0·267
Di*iso*butyl	116·7	417·5	0·280
Benzene	71·2	256·1	0·278
Fluorobenzene	75·1	271·2	0·277
Chlorobenzene	84·4	307·8	0·274
Bromobenzene	88·3	323·5	0·273

Formulæ of the type of equation (1) have been suggested by earlier workers. Thus van der Waals (*Z. physikal. Chem.*, 1894, **13**, 695) gave the equation

$$V - v = mV_c(1 - T_r)^{\frac{1}{3}} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

based on the theory of corresponding states. Here V and v are the specific volumes of vapour and liquid, respectively. Verschaffelt

(Commun. of Leiden, No. 28, 1896) advanced the general formula

$$D - d = mD_c(1 - T_r)^n \quad . \quad . \quad . \quad . \quad . \quad (6)$$

making $n = 0{\cdot}367$ for carbon dioxide. Goldhammer (*Z. physikal. Chem.*, 1910, **71**, 577) tested this formula on Young's density data, using $n = 1/3$ with fairly satisfactory results. It is readily shown that the exponent 3/10 gives results in better agreement with the available data than does Goldhammer's exponent 1/3, for $(D - d)^{10/3}$ is a linear function of temperature (see Table VI), as it should be according to equation (4), whereas $(D - d)^3$ exhibits a temperature coefficient which definitely increases with rise of temperature.

TABLE VI.

t.	$D-d$.	$(D-d)^{10/3}$.	Temp. coeff. $\times 10^5$.	$(D-d)^3$.	Temp. coeff. $\times 10^5$.
			Ether.		
0°	0·7354	0·3589		0·3976	
			186		185
40	0·6857	0·2844		0·3237	
			179		188
80	0·6286	0·2129		0·2484	
			197		212
120	0·5471	0·1340		0·1638	
			190		216
160	0·4256	0·0580		0·0771	
			186		231
180	0·3133	0·0209		0·0308	
			Ethyl acetate.		
0°	0·9243	0·7691		0·7896	
			319		297
40	0·8754	0·6416		0·6709	
			309		294
80	0·8210	0·5180		0·5532	
			302		294
120	0·7580	0·3972		0·4356	
			310		312
160	0·6775	0·2730		0·3109	
			314		331
200	0·5630	0·1473		0·1785	
			308		358
240	0·3279	0·0243		0·0353	

Summary.

1. The variation of density with temperature from the freezing point to the critical point is represented accurately for normal liquids by the equation $D - d = D_0(1 - T/T_c)^{3/10}$, where D and d are the densities of the liquid and saturated vapour, respectively, at $T°$ Abs.

2. This equation also holds for associated liquids over the lower part of the temperature range, and in some cases nearly to the critical point.

3. The "zero volume," V_0, obtained by dividing the molecular weight by the constant D_0, is nearly proportional to the critical volume for a large number of substances.

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CCXXXIV.—*Molecular Volumes at Absolute Zero. Part II. Zero Volumes and Chemical Composition.*

By SAMUEL SUGDEN.

IT has been shown (preceding paper) that the influence of temperature on the density of a liquid is represented accurately by the equation

$$D - d = D_0(1 - T/T_c)^{3/10} . \quad . \quad . \quad . \quad . \quad (1)$$

where D and d are the densities of the liquid and its saturated vapour, respectively, at a temperature T, and T_c is the critical temperature. The constant D_0 is the density the liquid would have at absolute zero if equation (1) still held; this assumption is probably not far from the truth, since the coefficient of expansion decreases continually as the temperature falls and is already small at the freezing point. In general, equation (1) gives values for D_0 which are about 20% greater than the density at 0°, so that if sufficiently accurate density data over a wide range of temperatures are available, the extrapolation seems to be justifiable.

By dividing this constant into the molecular weight one obtains the "zero volume," V_0, *i.e.*, the molecular volume of a supercooled liquid at absolute zero; this appears to be a very significant constant, for the form of equation (1) shows that zero volumes are proportional to the molecular volumes for a series of liquids at the same reduced temperature, *i.e.*, they are corresponding volumes. It has also been shown in Part I that zero volumes are nearly proportional to critical volumes in a number of cases in which the latter constant has been determined with accuracy.

It will now be shown that zero volumes are an additive function of chemical composition, and can be predicted with considerable accuracy for a large number of substances by adding together suitable constants for the atoms and structures present in the molecule. In the tables, the zero volumes of 284 substances are recorded and compared with the values obtained by adding the constants given in Table II. For 236 substances, or 82% of the number studied, the difference between the extrapolated and the calculated values does not exceed 2%.

The method by which D_0 is calculated from a range of density observations is outlined in Part I (p. 1781). It is obvious that the accuracy of the value found will depend on the accuracy and temperature range of the data employed. For most of the substances studied, densities accurate to 1 part in 1000 parts over a range of 40° or more have been used, and it is estimated that the maximum error in the calculation of D_0 is considerably less than $\frac{1}{2}$%. In a

few cases, the available observations covered a smaller temperature range, and the values of V_0 found may therefore be burdened with a larger error of calculation; these are indicated in the tables by parentheses.

(2) *Evaluation of Constants.*

The first evidence that zero volumes are simply related to chemical composition is given by the fact that position isomerides give nearly the same value for this constant. Some examples are quoted in Table I, and others will be found in the tables which follow.

TABLE I.

Position Isomerides.

$C_2H_4O_2$.	V_0.	C_8H_{10}.	V_0.
Methyl formate	46·7	Ethylbenzene	(99·3)
Acetic acid	46·7	*o*-Xylene	(98·9)
		m- ,,	(99·1)
$C_9H_{18}O_2$.		*p*- ,,	(100·7)
Ethyl *n*-heptoate	149·6	$C_8H_{10}O$.	
d-β-Butyl *n*-valerate	150·8	Phenetole	105·5
d-β-Hexyl propionate	149·7	*m*-Tolyl methyl ether	(103·9)
d-β-Heptyl acetate	150·5	*p*- ,, ,, ,,	(104·0)

It was next found that several homologous series (hydrocarbons, alkyl halides, ethers, esters, ketones, aldehydes, and amines) gave very nearly a constant difference in zero volumes for a difference in composition of CH_2; the values found for this constant ranged from 14·2 to 14·9 in different series with a weighted mean of $CH_2 = 14·5$. From this value, the constant for hydrogen was obtained by subtracting nCH_2 from a series of observations for the paraffins C_nH_{2n+2}, the mean value being H = 6·7, whence C = 1·1. These fundamental constants were then employed to evaluate the constants for other elements and structures.

It soon became apparent that the analysis of zero volumes could be carried out with the same simplicity as is met with in the case of the parachors (Sugden, J., 1924, **125**, 1177). With one or two exceptions (see p. 1796), the same constant serves for a particular atom in all its compounds, and the same constant for a particular structure, no matter what elements are taking part in it. Thus a double bond has the same value in ethylene derivatives, ketones, esters, and benzene derivatives; the last can all be expressed satisfactorily on the basis of the Kekulé formula. The most probable values for a number of atomic and structural constants are collected in Table II.

A clear distinction is also shown between the two types of double bond which have already been differentiated by means of the parachor (Sugden, Reed, and Wilkins, J., 1925, **127**, 1525). This

TABLE II.

Atomic and Structural Constants.

Atomic constants.		Atomic constants.		Structural constants.	
H	= 6·7	I	= 28·3	Triple bond	= 15·5
C	= 1·1	P	= 12·7	Double bond	= 8·0
N	= 3·6	S	= 14·3	3-Membered ring	= 4·8
O	= 5·0	O (in alcohols)	= 3·0	4-Membered ring	= 3·2
F	= 10·3	N (in amines)	= 0·0	5-Membered ring	= 1·8
Cl	= 19·3			6-Membered ring	= 0·6
Br	= 22·1			Semipolar double bond	= 0·0

is demonstrated by the data in Table III, in which the column headed ΣV_0 gives the sum of the atomic and structural constants for the substance considered except that for the linkage to be determined. By subtracting ΣV_0 from V_0 (obs.) the value shown in the last column for each type of double bond is obtained. It will be seen that, whilst a non-polar double bond gives a nearly constant increase of 8·0 c.c. in the zero volume, a semipolar double bond gives a constant which fluctuates about a value of zero.

TABLE III.

(i) Non-polar double bonds.

Substance.	Formula.	V_0 (obs.).	ΣV_0.	Double bond.
Ethylene	C_2H_4	37·4	29·0	8·4
Propylene	C_3H_6	51·7	43·5	8·2
Benzene	C_6H_6	71·2	47·4	7·9×3
Toluene	C_7H_8	86·7	61·9	8·3×3
Acetone	C_3H_6O	56·0	48·5	7·5
Acetylacetone	$C_5H_8O_2$	84·5	69·1	7·7×2
Methyl formate	$C_2H_4O_2$	56·7	39·0	7·7
Ethyl acetate	$C_4H_8O_2$	76·4	68·0	8·4

(ii) Semipolar double bonds.

Thionyl chloride	$SOCl_2$	58·0	58·1	−0·1
Sulphuryl chloride	SO_2Cl_2	62·6	63·1	−0·25×2
Methyl sulphate	$C_2H_6SO_4$	78·5	75·9	+1·3×2
Ethyl sulphite	$C_4H_{10}SO_3$	101·1	100·9	+0·2
Ethyl ethanesulphonate	"	96·7	"	−2·1×2
Ethyl sulphate	$C_4H_{10}SO_4$	107·3	103·9	+1·7×2
Nitrobenzene	$C_6H_5NO_2$	87·0	85·8	+1·2
Phosphorus oxychloride	$POCl_3$	73·4	75·4	−2·0
Ethyl phosphate	$C_6H_{15}PO_4$	140·5	139·6	+0·9
Phenyl phosphate	$C_{18}H_{15}PO_4$	(230·2)	226·8	+3·4
Nitric acid	HNO_3	32·7	33·3	−0·6
Sulphuric acid	H_2SO_4	47·1	47·7	−0·3×2
Perchloric acid	$HClO_4$	45·7	46·0	−0·1×3

It is noteworthy that the existence of the two types of double bond is now demonstrated by three independent lines of experimental evidence: (1) The different effect produced by these linkages on the parachor (Sugden, Reed, and Wilkins, *loc. cit.*), (2) the evidence from the optical activity of certain sulphur compounds which contain semipolar double bonds (Phillips, J., 1925,

127, 2552; 1926, 2079; this vol., p. 188), and (3) the effect of these two linkages upon the zero volume. The last of these methods has the advantage that it is applicable to associated liquids and shows (compare Table III) that free nitric, sulphuric, and perchloric acids contain, respectively, one, two, and three semipolar double bonds in accordance with the requirements of the octet theory of valency.

(3) *Normal Liquids.*

In this and the following section a comparison is made between the values of V_0 (obs.) derived from the density data and the predicted figure, V_0 (calc.), obtained by adding together the constants recorded in Table II. The column headed "Observer" gives initials only; full references are given on p. 1797.

Table IV gives the data for hydrocarbons.

TABLE IV.

Hydrocarbons.

Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %
1. Acetylene	C_2H_2	M. & W.	31·6	31·1	−1·6
„	„	Math.	32·0	„	−2·8
2. Ethylene	C_2H_4	M. & W.	37·4	37·0	−1·1
3. Ethane	C_2H_6	„	41·4	42·4	+2·4
4. Allylene	C_3H_4	„	44·3	45·6	+2·9
5. Propylene	C_3H_6	„	51·7	51·5	−0·4
6. Propane	C_3H_8	„	56·2	56·9	+1·3
7. *n*-Butane	C_4H_{10}	Wiss.	69·6	71·4	−2·6
8. *n*-Pentane	C_5H_{12}	Y.	83·9	85·9	+2·4
9. *iso*Pentane	„	„	86·1	„	−0·2
10. Benzene	C_6H_6	„	71·2	71·4	+0·3
„	„	P.	70·6	„	+1·2
11. Methyl*cyclo*pentane	C_6H_{12}	K.	(88·3)	88·8	+0·6
12. *cyclo*Hexane	„	J.	86·7	87·6	+1·0
„	„	Y.	86·0	„	+1·8
13. *n*-Hexane	C_6H_{14}	„	100·8	100·4	−0·4
14. Di*iso*propyl	„	„	99·9	„	+0·5
15. Toluene	C_7H_8	„	86·7	85·9	−0·9
„	„	P.	86·2	„	−0·3
16. Methyl*cyclo*hexane	C_7H_{14}	K.	102·6	102·1	−0·5
17. *n*-Heptane	C_7H_{16}	Y.	115·7	114·9	−0·7
„	„	P.	116·2	„	−1·2
18. Ethylbenzene	C_8H_{10}	„	(99·3)	100·4	+1·1
19. *o*-Xylene	„	„	(98·9)	„	+1·5
20. *m*- „	„	„	(99·1)	„	+1·3
21. *p*- „	„	„	(100·7)	„	−0·3
22. 1 : 1-Dimethyl*cyclo*hexane	C_8H_{16}	K.	(117·4)	116·6	−0·7
23. *n*-Octane	C_8H_{18}	Y.	130·8	129·4	−1·0
24. Di*iso*butyl	„	„	130·9	„	−1·1
25. *ψ*-Cumene	C_9H_{12}	P.	113·4	114·9	+1·4
26. Cumene	„	„	(113·8)	„	+1·0
27. Mesitylene	C_9H_{12}	P.	115·0	114·9	−0·1
28. *n*-Propylbenzene	„	„	(113·8)	„	+1·0
29. *p*-Cymene	$C_{10}H_{14}$	„	(128·6)	129·4	+0·7
30. *iso*Butylbenzene	„	„	(126·8)	„	+2·1

It may be noted that the densities of di*iso*butyl quoted by Landolt–Bornstein (4th edn., 1912, p. 154) are wrongly transcribed from Young's paper; the figures given are the densities of *cyclo*hexane which appear on the adjoining page.

Tables V, VI, VII, and VIII are self-explanatory. Some marked

Table V.

Halogen Derivatives.

	Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
31.	Carbon tetrachloride	CCl_4	Y.	77·4	78·3	+1·2
32.	Methylene iodide	CH_2I_2	P.	68·4	71·1	+3·9
33.	Acetylene tetrachloride	$C_2H_2Cl_4$	J.	87·7	92·8	+5·8
34.	„ tetrabromide	$C_2H_2Br_4$	„	100·9	104·0	+3·1
35.	Ethylene dichloride	$C_2H_4Cl_2$	„	62·8	67·6	+7·7
	„ „	„	P.	62·8	„	+7·7
36.	Ethyl iodide	C_2H_5I	„	64·2	64·0	−0·3
37.	*n*-Propyl bromide	C_3H_7Br	„	71·6	72·3	+1·0
38.	*p*-Dichlorobenzene	$C_6H_4Cl_2$	„	96·8	96·6	−0·2
39.	Fluorobenzene	C_6H_5F	Y.	75·1	75·0	−0·1
40.	Chlorobenzene	C_6H_5Cl	„	84·4	84·0	−0·4
	„	„	P.	83·2	„	+1·0
41.	Bromobenzene	C_6H_5Br	„	87·9	86·8	−1·3
	„	„	Y.	88·3	„	−1·7
42.	Iodobenzene	C_6H_5I	„	95·5	93·0	−2·6
	„	„	P.	94·1	„	−1·2
43.	*p*-Fluorobromobenzene	C_6H_4FBr	J.	90·8	90·4	−0·4
44.	*p*-Chlorobromobenzene	C_6H_4ClBr	S.	99·1	99·4	+0·3
45.	*p*-Chloroiodobenzene	C_6H_4ClI	„	102·9	105·6	+2·6
46.	*m*-Fluorotoluene	C_7H_7F	J.	90·2	89·5	−0·8
47.	*p*-Bromotoluene	C_7H_7Br	P.	102·3	101·3	−1·0
48.	*p*-Iodotoluene	C_7H_7I	S.	109·6	107·5	−1·9
49.	*n*-Octyl chloride	$C_8H_{17}Cl$	P.	140·4	142·0	+1·2
50.	*n*-Octyl bromide	$C_8H_{17}Br$	„	144·7	144·8	+0·1
51.	*n*-Octyl iodide	$C_8H_{17}I$	„	150·4	151·0	+0·4

Table VI.

Ethers.

	Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
52.	Ethylene oxide	C_2H_4O	M. & B.	37·7	38·8	+2·9
53.	Epichlorohydrin	C_3H_5OCl	J.	63·6	65·9	+3·6
	„	„	S. & W.	65·5	„	+0·7
54.	Ethyl ether	$C_4H_{10}O$	Y.	77·1	76·4	−0·9
55.	Paraldehyde	$C_6H_{12}O_3$	P.	(106·4)	102·6	−3·6
56.	Acetal	$C_6H_{14}O_2$	W.	112·2	110·4	−1·7
57.	Anisole	C_7H_8O	P., Sch.	90·8	90·9	+0·1
58.	Phenetole	$C_8H_{10}O$	„	105·5	105·4	−0·1
	„	„	B.	104·2	„	+1·2
59.	*m*-Tolyl methyl ether	„	P.	(103·9)	„	+1·5
60.	*p*- „ „ „	„	„	(104·0)	„	+1·4
61.	Veratrole	$C_8H_{10}O_2$	J.	106·1	110·4	+4·1
62.	Dimethylresorcinol	„	P.	109·2	„	+1·1
63.	Phenyl propyl ether	$C_9H_{12}O$	„	(117·9)	119·9	+1·7
64.	Phenyl *iso*propyl ether	„	„	(117·5)	„	+2·0
65.	Phenyl octyl ether	$C_{14}H_{22}O$	„	(188·7)	192·4	+1·9

deviations occur in compounds containing several halogen atoms, *e.g.*, ethylene dichloride (No. 35) and acetylene tetrachloride (No. 33). Since, however, carbon tetrachloride gives a satisfactory agreement, it is probable that these discrepancies are due to errors of observation. The long series of esters in Table VIII gives a test of accuracy of the additive properties of V_0 over a large range of molecular weight, and affords, in general, excellent support for the views now advanced.

TABLE VII.

Aldehydes and Ketones.

Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
66. Acetone	C_3H_6O	B.	56·0	56·5	+0·9
67. Methyl ethyl ketone	C_4H_8O	T. & J.	71·8	71·0	−1·1
68. Furfural	$C_5H_4O_2$	W.	68·5	68·1	−0·6
„	„	J.	68·7	„	−0·9
69. Acetylacetone	$C_5H_8O_2$	„	84·5	85·1	+0·7
70. Methyl propyl ketone	$C_5H_{10}O$	T. & J.	85·2	85·5	+0·4
71. Diethyl ketone	„	„	84·3	„	+1·4
72. Ethyl acetoacetate	$C_6H_{10}O_3$	P.	103·8	104·6	+0·8
73. Benzaldehyde	C_7H_6O	„	85·3	85·5	+0·3
74. Dimethylacetylacetone	$C_7H_{12}O_2$	„	111·6	114·1	+2·3
75. Dipropyl ketone	$C_7H_{14}O$	„	113·9	114·5	+0·5
76. Acetophenone	C_8H_8O	„	97·8	100·0	+2·2
77. Benzylideneacetone	$C_{10}H_{10}O$	„	123·8	123·6	−0·2
78. Benzophenone	$C_{13}H_{10}O$	„	141·3	143·5	+1·6

TABLE VIII.

Esters.

Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
79. Methyl formate	$C_2H_4O_2$	Y.	46·7	47·0	+0·7
80. Methyl acetate	$C_3H_6O_2$	„	61·1	61·5	+0·7
81. Ethyl formate	„	„	61·9	„	−0·7
82. Methyl propionate	$C_4H_8O_2$	„	75·5	76·0	+0·7
83. Ethyl acetate	„	„	76·4	„	−0·5
„ „	„	W.	75·9	„	+0·1
84. *n*-Propyl formate	„	Y.	76·7	„	−0·9
85. Methyl *n*-butyrate	$C_5H_{10}O_2$	„	90·7	90·5	−0·2
86. Methyl *iso*butyrate	„	„	90·6	„	−0·1
87. Ethyl propionate	„	„	90·9	„	−0·4
88. Propyl acetate	„	„	91·3	„	−0·9
89. Ethyl carbonate	$C_5H_{10}O_3$	S. R. & W.	98·2	95·5	−2·7
90. Methyl maleate	$C_6H_8O_4$	S. & Wh.	103·8	104·2	+0·4
91. Methyl fumarate	„	„	107·5	„	−3·2
92. *d*-β-Butyl acetate	$C_6H_{12}O_2$	P. & K.	106·1	105·0	−1·1
93. Methyl citraconate	$C_7H_{10}O_4$	S. & Wh.	117·1	118·7	+1·4
94. Methyl mesaconate	„	„	116·0	„	+2·3
95. Ethyl *cyclo*butanecarboxylate	$C_7H_{12}O_2$	S. & W.	108·5	109·3	+0·7
96. *d*-β-Butyl propionate	$C_7H_{14}O_2$	P. & K.	121·5	119·5	−1·7
97. Methyl benzoate	$C_8H_8O_2$	P.	(104·3)	105·0	+0·7
98. Phenyl acetate	„	„	104·8	„	+0·2
99. *d*-β-Butyl *n*-butyrate	$C_8H_{16}O_2$	P. & K.	134·4	134·0	−0·3
100. *d*-β-Hexyl acetate	„	„	135·5	„	−1·1

TABLE VIII (*contd.*)

	Substance.	Formula.	Observer.	V_0 (obs.).	V_0 calc.).	Diff., %.
101.	Ethyl 1-cyano*cyclo*-butane-1-carboxylate...	$C_8H_{11}O_2N$	S. & W.	122·5	122·8	+0·3
102.	Ethyl benzoate	$C_9H_{10}O_2$	P.	(119·0)	119·5	+0·4
103.	Ethyl *cyclo*propane-1 : 1-dicarboxylate ...	$C_9H_{14}O_4$	S. & W.	145·4	144·5	−0·6
104.	Ethyl *cyclo*propane-1 : 2-dicarboxylate ...	„	„	146·0	„	−1·0
105.	Ethyl *n*-heptoate	$C_9H_{18}O_2$	P.	149·6	148·5	−0·7
106.	*d*-β-Butyl *n*-valerate	„	P. & K.	150·8	„	−1·5
107.	*d*-β-Hexyl propionate ...	„	„	149·7	„	−0·8
108.	*d*-β-Heptyl acetate	„	„	150·5	„	−1·3
109.	Methyl cinnamate	$C_{10}H_{10}O_2$	S. & Wh.	127·5	128·6	+0·9
110.	Methyl *allo*cinnamate ...	„	„	124·3	„	+3·6
111.	*n*-Propyl benzoate	$C_{10}H_{12}O_2$	P.	(133·5)	134·0	+0·4
112.	*iso*Propyl benzoate	„	„	(136·6)	„	−1·9
113.	Ethyl *o*-toluate	„	„	(131·7)	„	+1·7
114.	Ethyl *p*-toluate	„	„	(133·3)	„	+0·6
115.	Ethyl phenylacetate	„	„	(130·2)	„	+2·8
116.	Ethyl *o*-methoxybenzoate	$C_{10}H_{12}O_3$	„	(135·1)	139·0	+2·9
117.	Ethyl *m*-methoxybenzoate	„	„	(137·1)	„	+1·4
118.	Ethyl anisate	„	„	(136·7)	„	+1·7
119.	Ethyl *cyclo*butane-1 : 1-dicarboxylate	$C_{10}H_{16}O_4$	S. & W.	158·4	157·4	−0·7
120.	*d*-β-Butyl *n*-hexoate	$C_{10}H_{20}O_2$	P. & K.	164·8	163·0	−1·2
121.	*d*-β-Hexyl *n*-butyrate ...	„	„	161·2	„	+1·2
122.	*d*-β-Heptyl propionate ...	„	„	164·7	„	+1·1
123.	*d*-β-Octyl acetate	„	„	164·6	„	+1·0
124.	Methyl α-bromocinnamate	$C_{10}H_9O_2Br$	S. & Wh.	138·7	136·0	−2·0
125.	Methyl α-bromo*allo*-cinnamate	„	„	140·4	„	−3·2
126.	Methyl β-bromocinnamate	„	„	139·5	„	−2·5
127.	Methyl β-bromo*allo*-cinnamate	„	„	142·4	„	−4·7
128.	Ethyl cinnamate	$C_{11}H_{12}O_2$	P.	141·9	143·1	+0·8
129.	Ethyl benzoylacetate ...	$C_{11}H_{12}O_3$	„	145·6	148·1	+1·7
130.	Ethyl phenylpropionate	$C_{11}H_{14}O_2$	„	146·7	148·5	+1·2
131.	*n*-Butyl benzoate	„	„	(147·4)	„	+0·7
132.	*iso*Butyl benzoate	„	„	(148·5)	„	±0·0
133.	Ethyl *p-iso*propylbenzoate	„	„	(149·5)	„	−0·7
134.	Ethyl caronate	$C_{11}H_{18}O_4$	S. & W.	171·4	173·5	+1·2
135.	*d*-β-Butyl *n*-heptoate ...	$C_{11}H_{22}O_2$	P. & K.	179·6	177·5	−1·2
136.	*d*-β-Hexyl *n*-valerate ...	„	„	179·0	„	−0·9
137.	*d*-β-Heptyl *n*-butyrate ...	„	„	179·7	„	−1·2
138.	*d*-β-Octyl propionate ...	„	„	177·6	„	−0·1
139.	Ethyl phthalate	$C_{12}H_{14}O_4$	P.	168·0	167·6	−0·3
140.	Ethyl terephthalate	„	„	168·2	„	−0·4
141.	*d*-β-Butyl *n*-octoate	$C_{12}H_{24}O_2$	P. & K.	195·5	192·0	−1·8
142.	*d*-β-Hexyl *n*-hexoate	„	„	194·0	„	−1·0
143.	*d*-β-Heptyl *n*-valerate ...	„	„	194·1	„	−1·1
144.	*d*-β-Octyl *n*-butyrate ...	„	„	194·2	„	−1·1
145.	Phenyl carbonate	$C_{13}H_{10}O_3$	S. R. & W.	157·2	153·5	−2·4
146.	Ethyl α-naphthoate	$C_{13}H_{12}O_2$	P.	151·9	153·9	+1·3
147.	Ethyl β-naphthoate	„	„	152·7	„	+0·8
148.	Phenyl *n*-heptoate	$C_{13}H_{18}O_2$	„	175·5	177·5	+1·2
149.	*d*-β-Butyl *n*-nonoate	$C_{13}H_{26}O_2$	P. & K.	207·3	206·5	−0·4
150.	*d*-β-Hexyl *n*-heptoate ...	„	„	207·6	„	−0·5

TABLE VIII (*contd.*)

	Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
151.	*d*-β-Heptyl *n*-hexoate ...	$C_{13}H_{26}O_2$	P. & K.	210·2	206·5	−1·8
152.	*d*-β-Octyl *n*-valerate	,,	,,	209·5	,,	−1·5
153.	*d*-β-Undecyl acetate	,,	,,	207·6	,,	−0·5
154.	*d*-β-Heptyl *n*-heptoate ...	$C_{14}H_{28}O_2$	,,	223·2	221·0	−1·0
155.	*d*-β-Octyl *n*-hexoate	,,	,,	223·3	,,	−1·1
156.	*d*-β-Undecyl propionate...	,,	,,	222·6	,,	−0·7
157.	*n*-Octyl benzoate	$C_{15}H_{22}O_2$	P.	(203·4)	206·5	+1·6
158.	Ethyl *cyclo*propane-1 : 1 : 2 : 2-tetracarboxylate	$C_{15}H_{22}O_8$	S. & W.	242·0	240·7	−0·5
159.	*d*-β-Butyl *n*-undecoate ...	$C_{15}H_{30}O_2$	P. & K.	237·2	235·5	−0·7
160.	*d*-β-Hexyl *n*-nonoate	,,	,,	236·3	,,	−0·4
161.	*d*-β-Heptyl *n*-octoate ...	,,	,,	238·1	,,	−1·1
162.	*d*-β-Octyl *n*-heptoate ...	,,	,,	237·0	,,	−0·7
163.	*d*-β-Undecyl *n*-butyrate...	,,	,,	236·5	,,	−0·4
164.	*d*-β-Butyl *n*-dodecoate ...	$C_{16}H_{32}O_2$	,,	252·1	250·0	−0·8
165.	*d*-β-Heptyl *n*-nonoate ...	,,	,,	252·2	,,	−0·9
166.	*d*-β-Octyl *n*-octoate	,,	,,	251·5	,,	−0·6
167.	*d*-β-Undecyl *n*-valerate ...	,,	,,	250·8	,,	−0·3
168.	*d*-β-Hexyl *n*-undecoate ...	$C_{17}H_{34}O_2$	,,	264·5	264·5	±0·0
169.	*d*-β-Octyl *n*-nonoate	,,	,,	266·8	,,	−0·9
170.	*d*-β-Undecyl *n*-hexoate ...	,,	,,	265·2	,,	−0·3
171.	*d*-β-Butyl myristate	$C_{18}H_{36}O_2$	,,	280·2	279·0	−0·4
172.	*d*-β-Hexyl *n*-dodecoate ...	,,	,,	278·7	,,	+0·1
173.	*d*-β-Heptyl *n*-undecoate	,,	,,	280·0	,,	−0·4
174.	*d*-β-Undecyl *n*-heptoate...	,,	,,	279·7	,,	−0·3
175.	*d*-β-Heptyl *n*-dodecoate...	$C_{19}H_{38}O_2$	,,	296·6	293·5	−1·0
176.	*d*-β-Octyl *n*-undecoate ...	,,	,,	294·2	,,	−0·2
177.	*d*-β-Butyl palmitate	$C_{20}H_{40}O_2$	,,	307·1	308·0	+0·3
178.	*d*-β-Hexyl myristate	,,	,,	307·3	,,	+0·2
179.	*d*-β-Octyl *n*-dodecoate ...	,,	,,	308·3	,,	−0·1
180.	*d*-β-Undecyl *n*-nonoate ...	,,	,,	307·7	,,	+0·1
181.	*d*-β-Heptyl myristate.....	$C_{21}H_{42}O_2$	,,	323·1	322·5	−0·2
182.	*d*-β-Butyl stearate	$C_{22}H_{44}O_2$	,,	334·7	337·0	+0·7
183.	*d*-β-Hexyl palmitate	,,	,,	337·0	,,	±0·0
184.	*d*-β-Octyl myristate	,,	,,	337·6	,,	−0·2
185.	*d*-β-Undecyl *n*-undecoate	,,	,,	335·1	,,	+0·6
186.	*d*-β-Heptyl palmitate.....	$C_{23}H_{46}O_2$	,,	352·3	351·5	−0·2
187.	*d*-β-Undecyl *n*-dodecoate	,,	,,	349·9	,,	+0·5
188.	*d*-β-Hexyl stearate	$C_{24}H_{48}O_2$	,,	360·6	366·0	+1·5
189.	*d*-β-Octyl palmitate	,,	,,	376·1	,,	−2·8
190.	*d*-β-Heptyl stearate	$C_{25}H_{50}O_2$	,,	377·2	380·5	+0·9
191.	*d*-β-Undecyl myristate ...	,,	,,	377·2	,,	+0·9
192.	*d*-β-Octyl stearate	$C_{26}H_{52}O_2$	,,	403·9	395·0	−2·2

Table IX contains the data for a number of nitro-compounds for which the structure $-N\begin{matrix}O\\O\end{matrix}$, containing one non-polar and one semipolar bond, has been assumed. If both the double bonds were non-polar, the value of V_0 (calc.) would have to be increased by 8·0 c.c. and would be much larger than the experimental figures.

The nitriles in Table X are assumed to have the structure $-C\equiv N$, which is confirmed by the good agreement between the observed and the calculated values. The same conclusion has been reached from a

study of the parachor of a number of nitriles (Sugden and Wilkins, *loc. cit.*), so that Langmuir's assumption of a special structure containing two kernels within one octet is unnecessary.

TABLE IX.

Nitro-compounds.

	Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
193.	Nitromethane	CH_3O_2N	W.	42·6	42·8	+0·5
	,,	,,	J.	42·9	,,	−0·2
194.	Ethyl nitrate	$C_2H_5O_3N$	W.	64·6	62·3	+3·5
195.	Nitrobenzene	$C_6H_5O_2N$	Y.	88·0	86·3	−1·9
	,,	,,	W.	86·0	,,	+0·4
196.	*m*-Fluoronitrobenzene	$C_6H_4O_2NF$	J.	89·7	89·9	+0·2
197.	*p*-Fluoronitrobenzene	,,	,,	89·0	,,	+1·0
198.	*o*-Chloronitrobenzene	$C_6H_4O_2NCl$	S. & W.	97·8	98·9	+1·1
199.	*m*- ,,	,,	,,	97·9	,,	+1·0
200.	*p*- ,,	,,	J.	102·1	,,	−3·2
201.	*o*-Bromonitrobenzene	$C_6H_4O_2NBr$	S. & W.	100·9	101·7	+0·8
202.	*m*- ,,	,,	,,	102·0	,,	−0·3
203.	*p*- ,,	,,	,,	103·3	,,	−1·6
204.	*o*-Nitrotoluene	$C_7H_7O_2N$	,,	99·3	100·8	+1·5
205.	*m*- ,,	,,	,,	100·0	,,	+0·8
206.	*p*- ,,	,,	,,	102·2	,,	−1·4

TABLE X.

Nitriles.

	Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
207.	Acetonitrile	C_2H_3N	W.	40·6	41·4	+1·9
208.	Malononitrile	$C_3H_2N_2$	W. & S.	52·3	54·9	+5·0
209.	Propionitrile	C_3H_5N	W.	55·3	55·9	+1·2
210.	Methyl cyanoacetate	$C_4H_5O_2N$	J.	74·4	75·0	+0·8
211.	Ethyl cyanoacetate	$C_5H_7O_2N$	,,	88·2	89·5	+1·5
	,, ,,	,,	W. & S.	87·8	,,	+1·9
212.	Benzonitrile	C_7H_5N	W.	85·6	84·9	−0·8
213.	Phenylacetonitrile	C_8H_7N	,,	97·1	99·4	+2·3
214.	*o*-Toluonitrile	,,	S. & W.	100·6	,,	−1·2
215.	*m*- ,,	,,	,,	100·3	,,	−0·9
216.	*p*- ,,	,,	,,	101·1	,,	−1·7

TABLE XI.

Phosphorus Compounds.

	Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
217.	Phosphorus trichloride	PCl_3	Th.	69·6	70·6	+1·4
218.	Phosphorus tribromide	PBr_3	S. R. & W.	78·6	79·0	+0·5
219.	Phosphorus oxychloride	$POCl_3$	,,	73·4	75·6	+3·0
220.	Triethyl phosphate	$C_6H_{15}O_4P$	,,	140·5	139·8	−0·5
221.	Triphenylphosphine	$C_{18}H_{15}P$	W. & S.	206·4	206·8	+0·2
222.	Triphenyl phosphate	$C_{18}H_{15}O_4P$	S. R. & W.	(230·2)	226·8	−1·5

Tables XI and XII record data for a number of compounds of phosphorus and sulphur. A good agreement between V_0 (obs.) and V_0 (calc.) is found in most cases, both in compounds containing only non-polar linkages and in those containing semipolar double bonds.

TABLE XII.

Sulphur Compounds.

Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
223. Thionyl chloride	$SOCl_2$	S. R. & W.	58·0	57·9	−0·2
224. Sulphuryl chloride	SO_2Cl_2	,,	62·6	62·9	+0·5
225. Sulphur monochloride ...	S_2Cl_2	J.	67·1	67·2	+0·1
226. Carbon disulphide	CS_2	,,	48·2	45·7	+5·1
227. Methyl thiocyanate	C_2H_3NS	W.	54·9	55·7	+1·5
228. Methyl sulphate	$C_2H_6O_4S$	S. R. & W.	78·5	76·7	−2·3
229. Thiophen	C_4H_4S	J.	63·5	63·3	−0·3
230. Ethyl sulphite	$C_4H_{10}O_3S$	W. & S.	101·1	100·7	−0·4
231. Ethyl ethanesulphonate	,,	,,	96·7	,,	+4·0
232. Ethyl sulphate	$C_4H_{10}O_4S$	S. R. & W.	107·3	105·7	−1·5
233. Thiophenol	C_6H_6S	W. & S.	85·6	85·7	+0·1
234. Diphenyl sulphide	$C_{12}H_{10}S$	P.	143·0	143·7	+0·5
235. Dibenzyl sulphide	$C_{14}H_{14}S$	,,	170·8	172·7	+1·1

(4) *Associated Liquids.*

It has been shown (preceding paper) that acetic acid and ethyl alcohol deviate from the requirements of equation (1) at high temperatures, but that at lower temperatures they give a satisfactory agreement. For acetic acid, in fact, the deviation only becomes appreciable in the neighbourhood of the critical temperature; it is therefore to be expected that the value of V_0 calculated from density observations at lower temperatures will be reproduced by adding together suitable constants from Table II. The data in Table XIII show that this is substantially true for a number of acids.

TABLE XIII.

Acids.

Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
236. Formic acid.....	CH_2O_2	W.	30·7	32·5	+5·8
237. Acetic acid	$C_2H_4O_2$	Y.	46·7	47·0	+0·7
238. Monochloroacetic acid ...	$C_2H_3O_2Cl$	J.	56·4	59·6	+5·7
239. Dichloroacetic acid	$C_2H_2O_2Cl_2$	,,	69·1	72·2	+4·4
240. Trichloroacetic acid	$C_2HO_2Cl_3$	,,	83·3	84·8	+1·8
241. Propionic acid	$C_3H_6O_2$	P.	60·8	61·5	+1·2
242. *n*-Heptoic acid	$C_7H_{14}O_2$	,,	118·3	119·5	+1·1
243. Nitric acid	HNO_3	V. & M.	32·7	33·3	+1·9
244. Sulphuric acid	H_2SO_4	W.	47·1	47·7	+1·3
245. Perchloric acid	$HClO_4$	Wi.	45·7	46·0	+0·7

For the alcohols, association appears to produce a small contraction in volume, and with the exception of methyl and ethyl alcohols the observed values are satisfactorily reproduced (Table XIV) by giving oxygen the value 3·0 in alcohols instead of the usual value O = 5·0. A somewhat larger contraction is found for amines (Table XV), for which N = 0 is used instead of 3·6 as in other nitrogen compounds. This contraction in zero volume is probably not a real change in volume but may be accounted for as follows. It seems probable from the behaviour of acetic acid and ethyl alcohol that equation (1) holds so long as the degree of association remains unchanged with increasing temperature, but that if the degree of association alters then the density decreases with temperature more rapidly than is predicted by this equation. For observations below the boiling point, the effect is small, and produces a small increase in the rate of change of density with temperature, which on extrapolation gives rather too high a value for the zero density, and consequently too small a value for the zero volume. This explanation is supported by the fact that methyl and ethyl alcohols, for which equation (1) holds up to temperatures well above the boiling points, do not exhibit this contraction, but give values for oxygen of about 5·0.

TABLE XIV.

Alcohols.

	Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
246.	Methyl alcohol	CH_4O	Y.	32·3	30·9	−4·3
247.	Ethyl alcohol	C_2H_6O	,,	46·8	45·4	−2·9
248.	Ethylene glycol	$C_2H_6O_2$	W.	48·4	48·4	±0·0
249.	*n*-Propyl alcohol	C_3H_8O	P.	60·6	59·9	−1·2
250.	*d*-Methylethylcarbinol	$C_4H_{10}O$	P. & K.	74·4	74·4	±0·0
251.	*d*-Methyl-*n*-propylcarbinol	$C_5H_{12}O$	,,	88·1	88·9	+0·9
252.	Phenol	C_6H_6O	P.	74·3	74·4	+0·1
	,,	,,	B.	74·3	,,	+0·1
253.	*d*-Methyl-*n*-butylcarbinol	$C_6H_{14}O$	P. & K.	102·4	103·4	+1·0
254.	*o*-Chlorophenol	C_6H_5OCl	B.	86·2	87·0	+0·9
255.	*o*-Cresol	C_7H_8O	,,	86·9	88·9	+2·3
256.	*m*- ,,	,,	,,	88·6	,,	+0·4
257.	*p*- ,,	,,	,,	89·5	,,	−0·7
258.	Benzyl alcohol	,,	P.	88·3	,,	+0·7
	,, ,,	,,	W.	87·9	,,	+1·1
259.	*d*-Methyl-*n*-amylcarbinol	$C_7H_{16}O$	P. & K.	116·2	117·9	+1·5
260.	Methyl salicylate	$C_8H_8O_3$	P.	106·6	108·0	+1·3
261.	Cinnamyl alcohol	$C_9H_{10}O$	,,	110·2	112·5	+2·1
262.	Ethyl salicylate	$C_9H_{10}O_3$	,,	122·3	122·5	+0·2
263.	*d*-Methyl-*n*-heptylcarbinol	$C_9H_{20}O$	P. & K.	145·3	146·9	+1·1
264.	Cuminol	$C_{10}H_{14}O$	P.	135·1	132·4	−2·0
265.	Thymol	,,	,,	130·4	,,	+1·8
266.	*d*-Methyl-*n*-octylcarbinol	$C_{10}H_{22}O$	P. & K.	159·7	161·4	+1·1
267.	*d*-Methyl-*n*-nonylcarbinol	$C_{11}H_{24}O$	,,	174·3	175·9	+0·9
268.	*d*-Methyl-*n*-decylcarbinol	$C_{12}H_{26}O$	,,	186·4	190·4	+2·3

TABLE XV.

Amines.

Substance.	Formula.	Observer.	V_0 (obs.).	V_0 (calc.).	Diff., %.
269. Ammonia	NH_3		19·1	20·1	+5·0
270. Methylamine	CH_5N	J.	33·7	34·6	+2·7
271. Dimethylamine	C_2H_7N	,,	50·1	49·1	−2·0
272. Ethylamine	,,	,,	48·2	,,	+1·8
273. Trimethylamine	C_3H_9N	,,	65·6	63·6	−3·0
274. *n*-Propylamine	,,	,,	62·7	,,	+1·4
275. Diethylamine	$C_4H_{11}N$	,,	78·0	78·1	+0·1
276. Piperidine	$C_5H_{11}N$	,,	79·7	79·8	+0·1
277. Aniline	C_6H_7N	Y.	77·7	78·1	+0·4
,,	,,	B.	76·8	,,	+1·7
278. *m*-Phenylenediamine	$C_6H_8N_2$	P.	82·5	84·8	+2·8
279. Triethylamine	$C_6H_{15}N$	J.	108·1	107·1	−0·9
280. Di-*n*-propylamine	,,	,,	108·0	,,	−0·8
281. *o*-Toluidine	C_7H_9N	P.	90·5	92·6	+2·3
282. Benzylamine	,,	,,	91·2	,,	+1·5
283. Dimethylaniline	$C_8H_{11}N$	,,	105·7	107·1	+1·3
284. Tripropylamine	$C_9H_{21}N$	J.	153·1	150·6	−1·7

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Summary.

(1) It has been shown that zero volumes can be predicted by adding together certain characteristic constants for the atoms and structures present in the molecule. Of the 284 compounds considered, 236 are within 2% and 149 within 1% of the calculated value. The agreement is not quite so good as is found with the parachor; the zero volume is, however, extrapolated from the

experimental data and is therefore subject to a greater error in its determination.

(2) Non-polar and semi-polar double bonds can be clearly distinguished by their effect upon the zero volume.

(3) The zero volumes of associated liquids, *e.g.*, alcohols and amines, can be predicted by making a small change in the values for oxygen and nitrogen.

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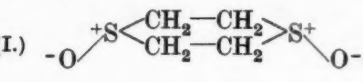
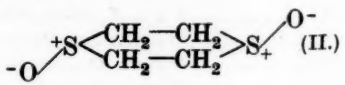
CCXXXV.—cis-trans-*Isomerism of Disulphoxides.*

By ERNEST VERE BELL and GEORGE MACDONALD BENNETT.

THE isolation of optically active ethyl *p*-toluenesulphinate (Phillips, J., 1925, **127**, 2552) and optically active sulphoxides of the type RR′SO (Harrison, Kenyon, and Phillips, J., 1926, 2079) proves that the three groups attached to the sulphur atom in these compounds do not lie in one plane with it. It follows that, if two sulphoxyl groups are present in a molecule, two isomerides should arise having the *cis*- and the *trans*-configuration, respectively. No such isomerism has hitherto been observed, although suitable disulphoxides have been known for half a century. We have therefore subjected two such cases to a closer investigation and have in each case isolated a pair of isomeric disulphoxides.

The so-called disulphoxides derived from the disulphides R·S·S·R′ are not in question, for it has become clear that they do not actually possess the disulphoxide structure R·SO·SO·R′, but are of the type R·S·SO_2·R′ (Smiles and Gibson, J., 1924, **125**, 176; Miller and Smiles, J., 1925, **127**, 224).

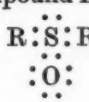
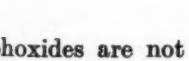
The simplest case is presented by the disulphoxides (I) and (II) of diethylene disulphide (1 : 4-dithian).

(I.)   (II.)

Here the plane of symmetry present in the molecule of each isomeride excludes the possibility of enantiomorphism. A disulphoxide of 1 : 4-dithian was isolated by Crafts (*Annalen*, 1862, **124**, 110; 1863, **125**, 123), which was soluble in water and separated from it in rhomb-shaped crystals. An examination of the mother-liquor from the crystallisation of this substance has now revealed the presence of an isomeride. The two disulphoxides decompose without melting, and their characterisation has depended on their

differences in solubility and in crystallographic properties. The α-isomeride is monoclinic and its solubility in 90% ethyl alcohol is less than one-fifth of that of the β-form, which is anorthic. The alternative formula $S<\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}>SO_2$, which might represent one of the isomerides as structurally isomeric, is inadmissible, for both the α- and the β-isomeride are readily reduced to the parent disulphide, a reaction characteristic of sulphoxides, but never shown by sulphones.

The configurations of these disulphoxides cannot be determined with certainty, but it may be tentatively assumed that the α-isomeride, being the less soluble, is the *trans*-form (II). Attempts to convert one isomeride into the other by heating in aqueous solution alone, or with acetic or hydrochloric acid of various concentrations, were unsuccessful. When heated with 5—20% hydrochloric acid, both disulphoxides behaved as peroxides, yielding dithian itself. The fact that it was not possible to bring about the interconversion of these isomeric disulphoxides is surprising, yet it is in agreement with the stability of the optically active sulphoxides, which showed no marked tendency to racemisation.

There is reason to suppose that the dissolution of an aldehyde or ketone in water involves the formation of a compound of the type $R{\cdot}C(OH)_2{\cdot}R'$, and with the older formulation of sulphoxides their ready solubility in water would by analogy have been attributed to the formation of a corresponding compound $R{\cdot}S(OH)_2{\cdot}R'$. If this were so, it would involve the rapid racemisation of active sulphoxides and the easy interconversion of *cis-trans*-isomerides in aqueous solution. On the other hand, from a consideration of the electronic formulæ it is clear that a compound $R{\cdot}S(OH)_2{\cdot}R'$ cannot exist as such, but only as the two ions:  and . Yet solutions of sulphoxides are not markedly alkaline, so that a complex, if it exists, must occur largely in some non-dissociated form. These considerations point to the following formula as a probable one:  (compare formulæ suggested for weak nitrogen bases by Moore and Winmill, J., 1912, **101**, 1635; Latimer and Rodebush, *J. Amer. Chem. Soc.*, 1920, **42**, 1419).

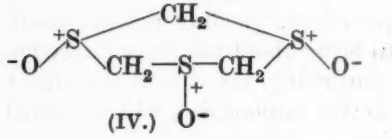
The disulphoxide derived from diethyldithiolethane,

$$CH_2(SEt){\cdot}CH_2{\cdot}SEt,$$

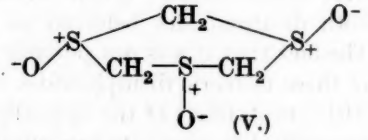
was described by Beckmann in 1878 (*J. pr. Chem.*, 1878, **17**, 409). We have examined the oxidation of the closely related dimethyl-

dithiolethane. The product of the reaction is a mixture of two isomeric disulphoxides, $Me{\cdot}SO{\cdot}C_2H_4{\cdot}SOMe$, the α-form, m. p. 163—164°, being less soluble in various solvents than the β-form, m. p. 128—130°. Both are readily reduced to the disulphide. One of these isomerides must be an inactive mixture (or compound) of two enantiomorphs, but it is not possible to discriminate between them. This pair of isomerides is closely analogous to the two diethiodides of the same disulphide which were recently described by Wedekind (*Ber.*, 1925, **58**, 2510).

It follows from the results now described that a cyclic trisulphoxide also should occur in two forms, and it is possible that the two isomeric trisulphoxides of trimethylene trisulphide obtained by Hinsberg (*J. pr. Chem.*, 1912, **85**, 1912; 1914, **89**, 547) are, in fact, the two substances (IV) and (V).



(IV.)



(V.)

The criticisms of Fromm and Schultis (*Ber.*, 1923, **56**, 937), however, suggest the advisability of a reinvestigation of this case.

We are indebted to Professor S. Smiles, F.R.S., for drawing our attention to the isomeric disulphoxides of thianthren (Fries and Vogt, *Ber.*, 1911, **44**, 756). The isomerism in this case is well established, but it has hitherto remained unexplained. It is evidently another example of the phenomenon under discussion.

EXPERIMENTAL.

Oxidation of 1 : 4-*Dithian by Hydrogen Peroxide.*—To a solution of dithian (10 g.) in glacial acetic acid (200 c.c.) at 0°, hydrogen peroxide (2 mols. of 30% aqueous solution), dissolved in an equal volume of acetic acid, was added, and the mixture kept for 24 hours. Most of the acetic acid and any trace of unchanged sulphide were then removed in a current of steam and the solution was evaporated to dryness three times to remove acetic acid (yield, 12·5 g. of crude disulphoxides). The product consisted mainly of the α-disulphoxide, which is undoubtedly that described by Crafts. Crystallisation of the crude mixture from 90% ethyl alcohol (400 c.c.) yielded this compound, and one further crystallisation from 50% ethyl alcohol (50 c.c.) gave the pure substance (7·8 g.) in rhomb- or hexagonal-shaped plates, decomp. 263° (uncorr.) (Found: C, 31·3; H, 5·4; *M*, cryoscopic in water, 142, 149. Calc.: C, 31·55; H, 5·3%; *M*, 152).

The substance is readily soluble in cold water and practically insoluble in absolute ethyl alcohol and other organic solvents. It crystallises in the monoclinic system, having $a : b : c = 1{\cdot}267 : 1 : 0{\cdot}979$; $\beta = 104°\ 3'$. Crystals of the habit shown in Fig. 1 were obtained by slow evaporation of an aqueous solution. The following is a list of the forms and the angular measurements observed with three crystals :

	a (100).	*m* (110).	*r* (101).	*R* (Ī01).	*q* (011).
ϕ	0° 0′	*50° 52′	0° 0′	180° 0′	*75° 40′
ρ	90° 0′	90° 0′	46° 18′	28° 32′	*45° 19′

The simpler rhomb-shaped crystals are developed on *R* bounded by *q* and *m*. The angle of the rhomb was observed under the microscope to be about 71° (calc., 71° 6′). The extinction on the face *R* is oblique. The position of the optic axes was not observed. The crystals had $d_4^{20°}$ (vac.) 1·570.

By fractional crystallisation of the material retained in the mother-liquor of this sulphoxide a small amount of another, more soluble substance was obtained, which crystallised in needles from absolute ethyl alcohol. The separation was facilitated by the fact that the two substances, although not very different in microscopic appearance in ordinary light, were sharply differentiated when seen between crossed Nicols. The second isomeride was best obtained thus : The crude mixture of disulphoxides (6·2 g.) was warmed with aqueous alcohol (90%, 200 c.c.), and then cooled in ice, and the solution was filtered. The solid residue (4·3 g.) was almost pure α-disulphoxide. The solution on evaporation left a residue (1·9 g.), which was boiled with enough absolute ethyl alcohol to dissolve about half of it. The solution was filtered and, on cooling, it deposited the β-*isomeride* (0·8 g.), which was pure after one further crystallisation (Found : C, 31·55; H, 5·2; *M*, 132, 144. $C_4H_8O_2S_2$ requires C, 31·55; H, 5·3%; *M*, 152).

β-*Dithian dioxide* separates from aqueous or absolute alcohol in elongated plates or flat needles, decomp. 235—250°. It crystallises in the anorthic system, having the angular elements *ab*, 105° 0′; *d*, 56° 17′; *e*, 127° 14′; *f*, 61° 44′; and *g*, 120° 59′. Crystals of the habit shown in Fig. 2 were obtained by slow crystallisation of an aqueous solution. The following forms and mean angular values were observed with three crystals :

	a (100).	*b* (010).	*c* (001).	*o* (111).
ϕ	0° 0′	*105° 0′	*241° 11′	*60° 28′
ρ	90° 0′	90° 0′	*40° 56′	*37° 29′

The extinction on *a* is at about 4° to the edge *ab*. The biaxial optic picture is seen in convergent light on face *a*, the optic axial

plane being nearly parallel to the edge *ab* and the acute bisectrix nearly normal to *a*. $d_4^{20°}$ (vac.) 1·554.

Determinations of Solubility and Proportion of the Isomerides present.—100 C.c. of ethyl alcohol dissolve less than 1 g. of the α-isomeride at the boiling point, and approximately 0·1 g. at 20°; the β-isomeride is three times as soluble in cold alcohol. The solubilities of the two substances in 90·7% ethyl alcohol were determined accurately in a thermostat at 22·0°. 100 C.c. of solution contained 0·38 g. of α-isomeride and 2·26 g. of β-isomeride. Use being made of these values, the proportion of the two isomerides present in the oxidation product was determined. The mixture (0·4006 g. made by means of hydrogen peroxide) was stirred for several hours in a closed bottle at 22·0° with 90·7% alcohol (25·0 c.c.); 10 c.c. of the solution then contained 0·0557 g. of material (mean

FIG. 1.

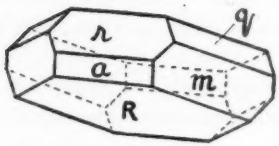
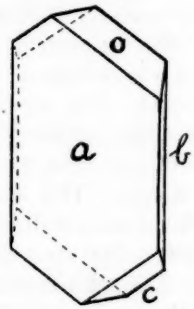


FIG. 2.



value). The influence of each on the solubility of the other being neglected, the two must be present in the proportion of 11·0% of the β- and 89·0% of the α-isomeride. A similar determination on the product of oxidation of dithian in ether by means of nitrous fumes showed the presence of 8·9% of the β-isomeride.

Reduction of the Disulphoxides.—A solution of the α-disulphoxide in acetic acid was boiled with addition of hydrochloric acid and zinc dust in excess. The solution when diluted and cooled deposited crystals of dithian (yield more than 50% of the theoretical), which was identified by direct comparison and the m. p. of a mixture with pure dithian. When the β-disulphoxide was reduced in the same way, dithian was again produced in quantity.

Attempted Interconversion of the Isomerides.—The α-disulphoxide was boiled for several hours in aqueous solution, and a known amount of ethyl alcohol then added. The weight of α-isomeride so recovered was exactly that expected, and therefore no conversion of α- into β-isomeride had occurred. The experiment was repeated with addition of acetic and dilute hydrochloric acids, but no positive

evidence of interconversion was obtained. When either isomeride was heated under reflux or in a sealed tube with hydrochloric acid (5—35%), dithian was always produced; it was identified as before. The second isomeride was in no case detected.

Oxidation of Dimethyldithiolethane.—The dimethyldithiolethane required was obtained very conveniently by methylating dithioglycol with methyl sulphate and aqueous alkali. To the disulphide (10 g.), dissolved in glacial acetic acid (100 c.c.) and cooled, hydrogen peroxide (20 g. of 29·2% aqueous solution) was added, and the mixture kept for 24 hours. The solution was then evaporated twice with addition of water, and the residue (12·5 g.) of mixed disulphoxides fractionally crystallised from ethyl alcohol, a mixture of ethyl alcohol and ethyl acetate (1 : 1), and finally from toluene or xylene. Two disulphoxides were thus separated, of which the α-isomeride was obtained pure more easily, as it was present in the larger quantity.

α-*Dimethylethylenedisulphoxide* crystallises from ethyl alcohol in monoclinic needles, m. p. 163—164° (Found: C, 31·1; H, 6·5; *M*, cryoscopic in camphor, 159. $C_4H_{10}O_2S_2$ requires C, 31·2; H, 6·5%; *M*, 154). It is readily soluble in water and moderately easily soluble in cold ethyl acetate or hot xylene.

β-*Dimethylethylenedisulphoxide* crystallises from alcohol or ethyl acetate in monoclinic bipyramids, m. p. 128—130° (Found: C, 31·0; H, 6·7%; *M*, 145). It is readily soluble in water or ethyl alcohol and sparingly soluble in ethyl acetate or hot toluene. The solubilities of the two isomerides in ethyl acetate at laboratory temperature are: α-, 0·16 g./100 c.c. (of solution); β-, 0·42 g./100 c.c. The melting point of the β-compound is not depressed by the addition of a little of the α-compound, although such mixtures have a considerable melting interval instead of a sharp melting point.

THE UNIVERSITY, SHEFFIELD. [*Received, May 17th*, 1927.]

CCXXXVI.—*Decomposition of some Halogenated Sulphides, and the Nature of the "Polymeric" Ethylene Sulphides.*

By ERNEST VERE BELL, GEORGE MACDONALD BENNETT, and ALFRED LOUIS HOCK.

THE union of an alkyl halide with an alkyl sulphide to produce a sulphonium salt is a reversible reaction, and unsymmetrical sulphonium halides may thus dissociate to yield compounds distinct from those used in their preparation:

$$R_2S + R'I \rightleftharpoons [R_2R'S]I \rightleftharpoons RR'S + RI$$

(Cahours, *Ber.*, 1875, **8**, 825; Klinger and Maassen, *Annalen*, 1889, **252**, 241).

An exactly analogous change was detected in an examination of some δ-substituted sulphides (this vol., p. 477) when a δ-bromobutyl sulphide was found to be transformed by internal salt formation into a cyclic sulphonium salt, $\left[\begin{matrix}CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2\end{matrix}\!\!>\overset{+}{S}\cdot C_4H_8\cdot OH\right]Br$, which dissociated, on heating, with liberation of the cyclic tetramethylene sulphide:

$$Br\cdot R - R - S\cdot R' \rightleftharpoons \left[\begin{matrix}R\\ |\\ R\end{matrix}\!\!>\overset{+}{S} - R'\right]Br \rightleftharpoons \begin{matrix}R\\ |\\ R\end{matrix}\!\!>S + R'Br.$$

It appeared probable that a similar tendency to the formation of sulphonium salts by self-addition would be a property common to all classes of halogenated sulphides. No such tendency has hitherto been recognised, but we find that some observations of our own on β- and γ-halogenated sulphides and one or two anomalies recorded in the literature may be explained as the results of such processes of reversible sulphonium salt formation.

The self-addition of a halogenated sulphide might evidently be intermolecular or intramolecular. The latter type of reaction involves ring closure, and it may be anticipated that it will only be in evidence when a five- or six-membered ring is concerned, as in the case of the δ-bromo-sulphide. An indication of intermolecular addition in a γ-halogenated sulphide was obtained when γγ′-dichlorodipropyl sulphide was converted by the action of sodium iodide into the corresponding di-iodo-sulphide. The latter decomposed, on keeping, with liberation of trimethylene iodide in quantity, whilst a dark, viscous material was deposited which contained ionic iodine and was probably a mixture of complex substances. This may be explained as follows:

$$2S(C_3H_6I)_2 \rightleftharpoons \left[\begin{matrix}\overset{+}{S}(C_3H_6I)_2\\ |\\ C_3H_6\cdot S\cdot C_3H_6I\end{matrix}\right]I \rightleftharpoons \begin{matrix}S\cdot C_3H_6I\\ |\\ C_3H_6\cdot S\cdot C_3H_6I\end{matrix} + C_3H_6I_2.$$

The more complex di-iodo-sulphide on the right may undergo further changes of the same kind so that a mixture of substances results.

It is known that most specimens of ββ′-dichlorodiethyl sulphide contain dithian (see, *e.g.*, Davies, J., 1920, **117**, 299), but the reason for its presence has never been elucidated. It has usually been regarded as an impurity introduced at the time of preparation, but there is now no doubt that the proportion of dithian in samples of dichlorodiethyl sulphide increases greatly with the time of keeping. The production of dithian can be explained as due to a series of

reactions involving both the intermolecular and the intramolecular type of addition, thus,

$$2S(C_2H_4Cl)_2 \rightleftharpoons \left[S<\begin{matrix}C_2H_4\cdot\overset{+}{S}(C_2H_4Cl)_2\\ C_2H_4Cl\end{matrix}\right]Cl \rightleftharpoons S<\begin{matrix}C_2H_4\cdot S\cdot C_2H_4Cl\\ C_2H_4Cl\end{matrix} + C_2H_4Cl_2$$

$$S<\begin{matrix}C_2H_4\\ C_2H_4\end{matrix}>S + C_2H_4Cl_2 \rightleftharpoons \left[S<\begin{matrix}C_2H_4\\ C_2H_4\end{matrix}>\overset{+}{S}\cdot C_2H_4Cl\right]Cl$$

ethylene dichloride being a second substance produced in the process. We have tested the truth of this scheme of reactions, as far as possible, and have directly confirmed the formation of both dithian and ethylene dichloride in quantity from pure dichlorodiethyl sulphide heated at 180° for 18 hours. A similar reaction doubtless occurs more slowly at the ordinary temperature. If these reactions are reversible at each stage (as shown), the action of ethylene dichloride upon dithian should conversely to some extent yield dichlorodiethyl sulphide, although the amount present in the final equilibrium mixture might be small. We find that dithian heated at 180° with an excess of ethylene dichloride yields a highly vesicant liquid, and the presence of dichlorodiethyl sulphide is proved by the isolation of the crystalline ββ′-diphenoxydiethyl sulphide (Helfrich and Reid, *J. Amer. Chem. Soc.*, 1920, **42**, 1208).

The curious observation of Davies (*loc. cit.*) that potassium cyanide acts on dichlorodiethyl sulphide to furnish the dinitrile, $CN\cdot CH_2\cdot CH_2\cdot S\cdot CH_2\cdot CH_2\cdot S\cdot CH_2\cdot CH_2\cdot CN$, is intelligible from the same point of view. This dinitrile is a by-product evidently derived from an intermediate mononitrile as follows :

$$2CN\cdot C_2H_4\cdot S\cdot C_2H_4Cl \rightleftharpoons \left[\begin{matrix}CN\cdot C_2H_4\cdot\overset{+}{S}\cdot C_2H_4\cdot S\cdot C_2H_4\cdot CN\\ C_2H_4Cl\end{matrix}\right]Cl \rightleftharpoons C_2H_4(S\cdot C_2H_4\cdot CN)_2 + C_2H_4Cl_2.$$

The formation and dissociation of a sulphonium salt also explains the anomaly noticed by Clarke (J., 1912, **101**, 1794) in the reaction of phenacyl bromide with dithian. The amount of ionic bromine, observed at intervals by titration, was found to rise at first as expected, but then diminished rapidly. This is clearly evidence of the opening of a ring as follows,

$$S<\begin{matrix}C_2H_4\\ C_2H_4\end{matrix}>S + COPh\cdot CH_2Br \rightleftharpoons \left[S<\begin{matrix}C_2H_4\\ C_2H_4\end{matrix}>\overset{+}{S}\cdot CH_2\cdot COPh\right]Br \rightleftharpoons S<\begin{matrix}C_2H_4\cdot S\cdot CH_2\cdot COPh\\ C_2H_4Br\end{matrix}$$

the bromo-sulphide on the right containing no ionic bromine.

The Nature of the "Polymeric" Ethylene Sulphides.—The reactions

discussed above throw a new light on the nature of the "polymeric" ethylene sulphides, which are produced in a variety of reactions, such as the action of alkali sulphides on ethylene dichloride, ethylene dibromide or dichlorodiethyl sulphide, and by the dehydration of monothioethylene glycol. It is probable that they are all mixtures of substances of high molecular weight having a long open-chain structure of the type $A(S{\cdot}C_2H_4)_n{\cdot}S{\cdot}B$, where A and B may be such groups as $-C_2H_4{\cdot}OH$, $-CH{:}CH_2$, or $-C_2H_4Br$ (Bennett and Whincop, J., 1921, **119**, 1861; *Nature*, 1926, **118**, 555; compare Staudinger, *Helv. Chim. Acta*, 1925, **8**, 67). The composition of these products is approximately that of a polymeride of ethylene sulphide (as is required by the formula provided that n be large), but it has long been known that variable amounts of bromine may be present (Crafts, *Annalen*, 1863, **128**, 220). The recent observations of Sir P. C. Rây and K. C. Bose-Rây (*J. Indian Chem. Soc.*, 1926, **3**, 75) support the idea of the occurrence of such long-chain bromopolyethylene polysulphides.

Two classes of "polymeric" ethylene sulphides were clearly distinguished by V. Meyer (*Ber.*, 1886, **19**, 3262): I, those which when heated did not yield dithian, and II, those which were readily degraded to dithian when heated alone or in solution in various solvents at high temperatures. The latter type of behaviour is to be expected in a bromo-polysulphide, owing to internal self-addition according to the scheme

$$R(S{\cdot}C_2H_4)_n{\cdot}S{\cdot}C_2H_4{\cdot}S{\cdot}C_2H_4Br \rightleftharpoons \left[R(S{\cdot}C_2H_4)_n{-}\overset{+}{S}{<}\begin{matrix}C_2H_4\\C_2H_4\end{matrix}{>}S\right]Br$$

$$\Downarrow$$

$$R(S{\cdot}C_2H_4)_n{\cdot}Br + S{<}\begin{matrix}C_2H_4\\C_2H_4\end{matrix}{>}S,$$

and repetitions of the process will liberate successive molecules of dithian, each cycle of changes being analogous to the reactions involved in the decomposition of dichlorodiethyl sulphide.

The existence of the "polymerides" of class I and their failure to yield dithian by a similar process will evidently be accounted for if they contain no halogen, since this is indispensable to sulphonium salt formation, and we find that, as far as evidence is available, "polymerides" which do not contain halogen do in fact belong to this class. Thus the material of Löwig and Weidmann (*Annalen*, 1840, **36**, 321) was found by Crafts (*loc. cit.*) to be free from halogen and to give no dithian on heating. We have confirmed the complete absence of halogen from a specimen of "polymeride" of class I prepared from ethylene dibromide, whilst products of class I from monothioethylene glycol were made from halogen-free materials

(J., 1922, **121**, 2144). These facts support our suggestion that it is the absence or the presence of halogen which determines the chemical differences between " polymerides " of class I and class II. In those of class I the terminal groups in the molecule are probably either $-C_2H_4\cdot OH$ or $-CH{:}CH_2$. Such substances would be likely to react with hydrogen bromide or with ethylene dibromide to yield halogenated polysulphides by such reactions as the following :

$R\cdot S\cdot C_2H_4\cdot OH + HBr = R\cdot S\cdot C_2H_4Br + H_2O$; $R\cdot S\cdot CH{:}CH_2 + HBr = R\cdot S\cdot C_2H_4Br$; $R\cdot S\cdot R' + C_2H_4Br_2 = R\cdot S\cdot C_2H_4Br + R'Br$.

The products would then be liable to the process of degradation with liberation of dithian. This anticipation also has been verified : " polymerides " of class I yield dithian when heated in boiling phenol, provided that hydrogen bromide or ethylene dibromide be added.

The simpler substances $S(C_2H_4\cdot OH)_2$, $C_2H_4(S\cdot C_2H_4\cdot OH)_2$, and $S(C_2H_4\cdot S\cdot C_2H_4\cdot OH)_2$ previously described (Bennett and Whincop, *loc. cit.*), which are not easily decomposed when heated alone, have now been found, as expected, to yield dithian readily when they are heated with a boiling solution of hydrogen bromide in phenol. These three dihydroxy-sulphides are the simplest members of a homologous series of substances, the higher members of which are doubtless present in " polymeric " ethylene sulphides of class I.

Experimental.

Action of Sodium Iodide on γγ'-Dichlorodipropyl Sulphide.—The pure dichloro-sulphide was heated in acetone solution with sodium iodide (3 mols.) until sodium chloride was no longer precipitated. The solution was concentrated, and the crude *γγ'-di-iododipropyl sulphide* thrown out as a heavy oil by dilution. This substance did not crystallise and could not be distilled without decomposition. When kept for several weeks at the ordinary temperature, the liquid deposited a dark resinous material which slowly hardened, but retained pockets of a heavy mobile oil. The solid could not be crystallised; it was partly soluble in water, the solution containing ionic iodine.

The oil was separated, and distilled at 120—130°/50 mm. It was identified as trimethylene di-iodide by direct comparison and by its ready conversion on heating with a solution of sodium phenoxide in phenol into αγ-diphenoxypropane, of which the m. p., 59—60°, was unaltered by admixture of an authentic specimen.

Decomposition of ββ'-Dichlorodiethyl Sulphide.—Freshly redistilled dichlorodiethyl sulphide (2·5 g.) was heated in a sealed tube for 18 hours in the vapour of boiling phenol. When the tube was

opened, a volatile liquid was noticed. The contents of the tube were mixed with an excess of aniline and heated at 100° for an hour and then at the boiling point for a further hour. The excess of aniline and the dithian were removed in a current of steam and the distillate was acidified to dissolve the aniline. The precipitate (0·5 g.; 50% of the theoretical yield) had m. p. 111°, not depressed by admixture of pure 1 : 4-dithian.

The residue from the steam distillation was extracted with ether, and the ether evaporated. The residual oil gave a crystalline sulphate when warmed with sulphuric acid (50%). This salt was crystallised from the filtered solution, and the base liberated from it by ammonia was crystallised from paraffin (b. p. 60°) and identified as ethylenediphenyldiamine, m. p. 60°, not depressed by admixture of an authentic specimen. This proves that the tube must have contained ethylene dichloride when opened.

The Action of Ethylene Dichloride upon Dithian.—Dithian (0·5 g.) and ethylene dichloride (5 c.c.) were heated in a sealed tube for 12 hours at 180°. Evaporation of the ethylene dichloride left a brown oil, which had a strong vesicant action. It was heated with an excess of alcoholic sodium phenoxide, and the solution was acidified and distilled in steam. The residual oil was removed in ether, and the latter evaporated. The viscous residue deposited crystals, which were drained on porous earthenware and recrystallised from paraffin of low b. p. This substance had m. p. 54°, not depressed by admixture of an authentic specimen of ββ′-diphenoxydiethyl sulphide. The two substances were also found by microscopic examination to crystallise identically from ethyl alcohol in bunches of needles with a straight extinction.

Degradation of "Polymeric" Ethylene Sulphide of Class I.—The specimen of "polymeride" was made by the action of alkali sulphide on ethylene dibromide, and had been freed from all trace of "polymeride" of class II by heating in phenol. It gave no dithian when dry-distilled or when heated in boiling phenol for several hours. Repeated tests proved the absence of halogen from this material.

The "polymeride" (30 g.) was heated at 130° for 1 hour with ethylene dibromide (18 g.; 1/5 mol.). Phenol (60 g.) was then added, and the mixture boiled for 3 hours. Addition of an excess of aqueous sodium hydroxide left a crystalline precipitate identified as dithian (6·7 g.).

The "polymeride" (15 g.) was boiled for 2 hours with phenol (60 g.) saturated with hydrogen bromide, and dithian was isolated as before (5 g.).

Production of Dithian from Simpler Hydroxy-sulphides.—Thio-

diglycol, ethylenebis-β-hydroxyethyl sulphide, and sulphidobis-β-hydroxydiethyl sulphide were each boiled for 2 hours with phenol saturated with hydrogen bromide, and the mixture was separated as before. In each case, dithian was identified, the yield from the last-named substance being nearly 50% by weight.

THE UNIVERSITY, SHEFFIELD. [*Received, May 31st*, 1927.]

CCXXXVII.—*Colour and Molecular Geometry. Part V. A Search for a Crucial Test of Colour Theories.*

By JAMES MOIR.

ANY theory of colour must, to be really successful, cover the whole field of absorbing substances—and this not merely qualitatively but quantitatively. It is not sufficient, for example, to establish a scheme in which most "coloured" (*i.e.*, absorbing) substances can be formulated with a little manipulation as "quinonoid" or as possessing alternate double and single linkages, inasmuch as there are plenty of exceptions to these schemes, namely, cases in which the amount of manipulation of the formula required to make it quinonoid is beyond belief (for example, *m*-aminophenol) or even beyond possibility (for example, the coloured solution of dihydroanthracene in concentrated sulphuric acid). It is also not sufficient to establish a scheme in which the various absorption bands of a substance examined in different media are related to one another in the same way as harmonics of a fundamental tone are, inasmuch as the connexion between the value of the fundamental and the chemical constitution has still to be discovered, also the reason why unexpected harmonics such as the 19th appear. A 19th harmonic is only credible if accompanied by the 7th, 13th, and 25th, or similar series; in other words, prime numbers as harmonics require a special explanation.

The author's theory, whilst admittedly a makeshift, is the only one capable of giving predictions of colour from constitution. Its use, however, is very greatly restricted by our lack of knowledge of the actual dimensions of many common molecules. Even the true configuration of benzene is still in doubt,* although the relation between anthracene and naphthalene is considered to be beyond doubt.

* Many writers appear to think that Körner's model is the same as Bragg's—which is not the case. The angle between adjacent carbon atoms in the skew-hexagon is 109° in Bragg's model and 90° in Körner's; consequently the representation of the position of the hydrogen atoms in Körner's model is quite erroneous.

The author therefore presents in this paper an experimental study of some of the oxygen derivatives of anthracene (together with a few of the corresponding derivatives of naphthalene) with the view of providing data for a crucial test of his own and other colour theories, a test founded on the fact that there is hardly any dispute as to the size and spatial configuration of the anthracene and naphthalene molecules.

Tables I and Ia contain the author's observations of the positions of the bands of these oxygen derivatives, made in dilute aqueous sodium hydroxide solution, in presence of sodium sulphite to prevent aërial oxidation.

TABLE I.

Absorption of Hydroxy-derivatives of Anthracene in Excess of Alkali.

	Central λ (in $\mu\mu$) of chief band.	Fainter bands.
1-Hydroxy-9 : 10-dihydroanthracene *	312	Nil.
1-Hydroxyanthracene (α-anthrol)	364	347, 410 broad
2-Hydroxyanthracene (β-anthrol)	335	Nil.
9-Hydroxyanthracene (anthranol)	378	,,
1 : 9-Dihydroxyanthracene (α-hydroxyanthranol)	490	460
2 : 9-Dihydroxyanthracene (β-hydroxyanthranol A)	476	447
3 : 9(or 2 : 10)-Dihydroxyanthracene (β-hydroxyanthranol B)	510	480
1 : 5-Dihydroxyanthracene (rufol)	371	354, 420 broad
2 : 6-Dihydroxyanthracene (flavol)	345	312, 378 broad
2 : 7-Dihydroxyanthracene	390	Nil.
9 : 10-Dihydroxyanthracene (anthraquinol)	495 broad	,,
1 : 5 : 9-Trihydroxyanthracene (anthrarufinanthranol)	427	370
1 : 2 : 10-Trihydroxyanthracene (deoxyalizarin)	480	Nil.
2 : 6 : 9-Trihydroxyanthracene (anthraflavinanthranol)	416	490, 515
2 : 7 : 9-Trihydroxyanthracene (*iso*anthraflavinanthranol)	492	466
2 : 9 : 10-Trihydroxyanthracene (β-hydroxyanthraquinol)	575	685
2 : 6 : 9 : 10-Tetrahydroxyanthracene (hydroanthraflavin)	486	454
1-Hydroxyanthraquinone	480	500
2-Hydroxyanthraquinone	470	495
1 : 2-Dihydroxyanthraquinone (alizarin)	613	568, 523
1 : 4-Dihydroxyanthraquinone (quinizarin)	595	552, 516
1 : 5-Dihydroxyanthraquinone (anthrarufin)	470	500
2 : 6-Dihydroxyanthraquinone (anthraflavin)	430	400, 485
2 : 7-Dihydroxyanthraquinone (*iso*anthraflavin)	475	390, 500

* The author finds that 1-hydroxy-9 : 10-dihydroanthracene (contrary to the statements of Liebermann, *Annalen*, 1882, **212**, 15, and Pleus, *Ber.*, 1902, **35**, 2928) is a phenolic substance closely resembling the cresols and has no colour in alkali. The author's specimen was made by sodium reduction of α-anthrol and agreed in appearance and melting point with the data in the literature.

TABLE Ia.

Absorption of some Corresponding Naphthalene Derivatives in Excess of Alkali.

	Central λ (in μμ) of chief band.	Fainter bands.
1-Hydroxynaphthalene	330	Nil.
2-Hydroxynaphthalene	349	,,
1 : 5-Dihydroxynaphthalene	350	,,
2 : 6-Dihydroxynaphthalene	340	356
2 : 7-Dihydroxynaphthalene	338	393
5-Hydroxy-1 : 4-naphthaquinone (juglone)	510	570
5 : 6-Dihydroxy-1 : 4-naphthaquinone (naphthazarin)	619	571

TABLE II.

Sulphonates in Aqueous Alkali.

Name.	Position of bands.
Anthraquinone-1-sulphonate	340 and 385
Anthraquinol-1-sulphonate	493 and 515
Anthranol-1-sulphonate	385 and 363
Anthracene-1-sulphonate	383, 364, 345, 326, and 308
Anthraquinone-1 : 5-disulphonate	333 and 420
Anthraquinol-1 : 5-disulphonate	491, 533, and 590
Anthranol-1 : 5-disulphonate	432, 460, and 490
Anthracene-1 : 5-disulphonate	389, 370, 350, and 305

The first point to be noted from the observations is the very interesting one that both of the anthrols and both of the symmetrical anthradiols are *visibly* coloured in moderately concentrated (N/500) solution, whereas the corresponding derivatives of naphthalene, all of which have absorption bands situated below λ 390 (the usually accepted lower limit of human vision), are not coloured in alkaline solution unless the solutions are very concentrated (over N/10). The α-compounds are more highly coloured than the β-compounds.

The second point is that the behaviour of the 1 : 5-dihydroxy-compounds is almost the same as that of the 1-hydroxy-compounds and that the 2 : 6-dihydroxy-compounds resemble the 2-hydroxy-compounds in behaviour. This symmetry clearly points to an influence of the centre (or the central plane) of the molecule on the height of colour.

The third point is the high colour (λ above 470) produced when one hydroxyl group is present in the 9-position. All the anthranols and anthraquinols show this, and, as is well known, all the hydroxyanthraquinones can be formulated in an alternative form with an OH-group in position 9. Usually the anthranol has a similar colour to that of the anthraquinone. This high colour is not easy to explain on any theory of colour.

The fourth point is that the highest colours of all occur in 2 : 9 : 10-, 1 : 2 : 9 : 10-, and 1 : 4 : 9 : 10-compounds (the 1 : 9 : 10-compound, α-hydroxyanthraquinol, could not be obtained). This is evidently due to superposition of effects due to the 9 : 10 arrangement—in itself capable of giving a red colour—on effects due to the co-operation of hydroxyl and the anthracene skeleton—in itself capable of giving a yellow colour, as shown above.

The last point is that the phenomena are almost exactly duplicated in the naphthalene series, so that the third ring in anthracene is of little significance. Thus juglone resembles erythrohydroxyanthraquinone, naphthazarin resembles alizarin, and all the mono- and di-hydroxynaphthalenes examined resemble the corresponding derivatives of anthracene. Nevertheless, anthraquinol (red in alkali) does not closely resemble 1 : 4-dihydroxynaphthalene in colour, although the alkaline solution of the latter compound is yellow (in presence of reducing agents to avoid oxidation), in contradistinction to that of ordinary quinol. 9 : 10-Anthraquinol in alkali absorbs from λ 520 to λ 470, 1 : 4-naphthaquinol at about λ 400, and quinol at λ 316.*

Those who have followed the author's attempts to find a theory of colour will remember that six years ago he put forward a factorial scheme whereby 90% of the data for dicyclic coloured substances could be correctly predicted (J., 1921, **119**, 1654), and later he showed that alteration of the angle between the rings is the reason why dicyclic coloured substances linked by carbon have lower colours than the corresponding substances in which nitrogen or oxygen forms the joint between the rings.

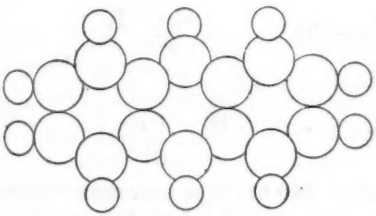
Further consideration shows that this scheme must sometimes break down when there is more than one joint, and this merely because the two joints cannot approach one another closely when one of them is carbon with its comparatively severe bend of 109°. Consequently, the calculated values for dihydroxyxanthhydrol and dihydroxyacridine are slightly incorrect (−3%), whereas those for dihydroxyanthracene, dihydroxyacridone, and dihydroxyxanthone are seriously incorrect (−12 to −25%). This means that the factor 0·65 used for calculating linkage by carbon can only be used once, so that if there is linkage by a second atom (in the ortho-position to the first linkage, of course) it occurs in such a way as to keep the molecule as flat as possible. Bragg's model for anthracene is an example, for, if my 1921 theory had been entirely correct, the anthracene model resulting would have been "buckled" in the

* If these effects are merely due to "loading" of quinol with one or with two benzene rings respectively, they are much the largest loading effects known.

middle, this being the only way in which both the central carbon atoms could make the normal (109°) angle with both rings.

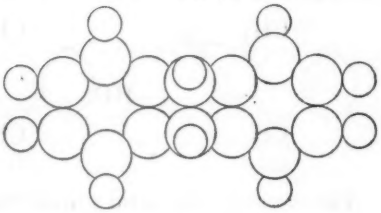
Figs. 1 and 2 represent two possible ways in which Bragg's measurements may be satisfied without any "buckling." Fig. 1, being without a cross bond, really represents dihydroanthracene, but is Bragg's own original diagram, with the β-hydrogen atoms put in the same plane as the β-carbon atoms. Fig. 2 shows the cross bond of anthracene as part of a Dewar–Ingold benzene model (triangular prism). Both models measure 11·18 Å. by 6·00 Å. The dimension 11·18 Å. of anthracene is made up of two ordinary benzene rings each of width 2·57 Å., one central ring of width 2·50 Å., two halves of a carbon atom, equal to 1·54 Å., and two hydrogen atoms, equal to 2·00 Å. The other dimension (vertical) is made up of $2{\cdot}57 \div (\sqrt{3}/2)$ (from the properties of a hexagon), plus two halves of a carbon atom, plus the projection of two hydrogen atoms lying

Fig. 1.



Anthracene (*Bragg*).
Dihydroanthracene (*Moir*).

Fig. 2.



Anthracene (*Moir*).

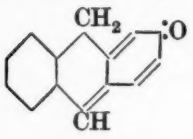
at 109° to the plane of the paper containing the β-carbon atoms. Similarly, if the middle ring be removed, the diagram agrees exactly with that of naphthalene $[(2 \times 2{\cdot}57) + (2 \times 0{\cdot}77) + 2{\cdot}0 = 8{\cdot}68$ for the length, whilst the breadth remains at 6·00 as in anthracene], these dimensions being exactly those given by Bragg. Inferentially also, the dimensions of the benzene molecule become, in this scheme, 6·11 Å. × 6·00 Å., a much closer approach to a true hexagon than one would expect at first sight from a molecule possessing a carbon skeleton of the skew-hexagon nature prescribed by Bragg.

Application of the Model to the Author's Colour Theory.

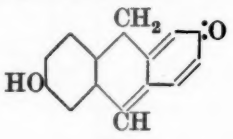
The extreme form of the author's theory, according to which the distance between the centres of the oxgyen atoms of the auxochromes decides the colour, is at once seen to be incorrect, because if this form of the theory were true, the substance flavol (2 : 6-dihydroxyanthracene), in which the centres of the oxygen atoms are as far apart as possible (10·6 Å. on the model), would possess an absorption

band at λ 850. Similarly, 2 : 6-dihydroxynaphthalene, which has, on the model, a distance of 8·1 Å. between its oxygen centres, would have a band at λ 650. Observation shows that the position of the chief band of both these substances is practically the same (λλ 345 and 340 respectively), both being pale yellow in alkaline solution. Light is now thrown on this obscurity by the fact that β-anthrol and β-naphthol have similar absorptions when examined in alkali solution (λλ 335 and 349 respectively). This shows that the colour vibration (colour orbit on the author's theory) is not from auxochrome to auxochrome, but is from *one* (that is to say, from either) auxochrome to a centre of force near the centre of the molecule.

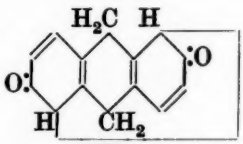
This idea can be correlated with the quinonoid theory as follows: β-Anthrol can be written as a quinonoid compound (I), and similarly flavol can be written as (II) but cannot be written so as to make the oxygens of *both* auxochromes quinonoid. I assume that such a formulation as (III) is patently absurd.



(I.)

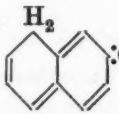


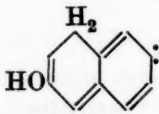
(II.)



(III.)

The cause of the band round about λ 340 in these four compounds (β-naphthol, 2 : 6-dihydroxynaphthalene, β-anthrol, and flavol) thus only concerns one ring. On my theory, λ 340 corresponds to a positive-centre distance of 4·36 Å. if both centres are oxygen atoms,* and about 4·2 Å. if one is a carbon atom. The latter distance on the model agrees with an orbit in which the electron grazes the oxygen atom of the auxochrome and at the other end of the ellipse passes through the double bond outside the para-carbon atom, the positive centres being the auxochrome oxygen and the para-carbon atom. Thus my theory leads to the same result as is reached by the quinonoid theory. The quinonoid formulæ for β-naphthol and 2 : 6-dihydroxynaphthalene involved are (IV) and (V), although they have also been formulated as ortho-quinonoid.

(IV.) 

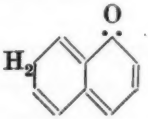
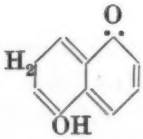
and 

(V.)

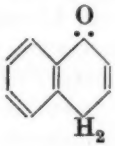
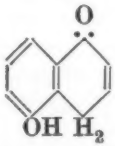
The α-compounds may now be considered. α-Naphthol and 1 : 5-dihydroxynaphthalene have much the same absorption as the

* For these calculations involving oxygen atoms alone, I find that the expression $\lambda = 82d - 20$ is sufficiently accurate.

β-compounds just discussed, *viz.*, an average value of 340 for λ. The corresponding distance is again 4·2 Å. and the corresponding quinonoid formulæ are :

(VI.)  and  (VII.)

Nevertheless, no distance can be found on the model in agreement with these suppositions. Agreement can, however, be obtained if the more customary quinonoid form be assumed, in which

(VIII.)  and  (IX.)

case the distance between oxygen and para-carbon agrees with what is required : the case thus becomes, in this instance, that of phenol with a "load."

The α-compounds of anthracene have a higher colour than those of naphthalene, due to bands at λλ 368 and 415 (on the average).

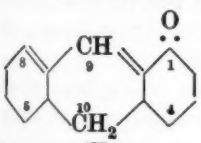
Alkaline solutions of 1-anthrol and of rufol (1 : 5-dihydroxy-anthracene) are yellow even in great dilution.

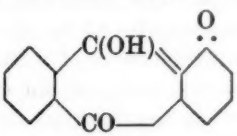
When, however, it comes to finding an explanation of this, it appears that Bragg's work is unfortunately less decisive as to the relative positions of α-groups than of β-groups.

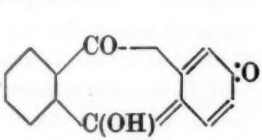
It is usually assumed, nevertheless (as on p. 1813), that α-groups lie in line with the benzene valencies, *i.e.*, inclined to the general plane of the model at the angle of 55° ($\sin^{-1}\sqrt{\frac{2}{3}}$) prescribed by the geometry of the skew-hexagon benzene model. An attempt to depict this *in plano* is shown in Figs. 1 and 2.

I find that an orbit round the α-oxygen and para-carbon atoms does not suit the colour, although the analogous supposition does suit in the case of the β-compounds. Neither does an orbit round the 1-α-oxygen and the 10-*meso*-carbon atom.

The only orbit which agrees is one which involves the double linkage lying between carbon atom 8 and its neighbour which links it to 9 in the quinonoid formula (X) for 1-anthrol.


(X.)


(XI.)


(XII.)

The centre of this unnumbered linking-carbon atom is at approximately the correct distance from the centre of the 1-oxygen atom to account on my theory for the observed band at λ 415 and the yellow colour.

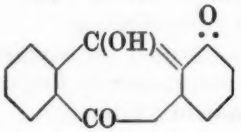
The Hydroxyanthraquinone Dyes.

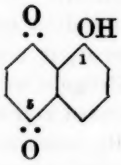
In explaining the colour of these dyes the author accepts the customary theory that the oxygen atoms attached at positions 9 and 10 compete with the hydroxylic oxygen atoms for a tautomerising hydrogen atom, as in the usual formulæ (XI and XII).

The tautomerism of the β-compounds is the ordinary quinonoid one, but in the α-compounds the chemical bonds cannot be arranged so as to show a tautomerism between 1- and 10-oxygens. This need not, however, deter us from conceiving the colour as being due to the movement of a single electron round these two oxygen atoms considered as positive centres—inasmuch as the case is similar to that of the "meta-quinonoid" coloured substances such as *m*-nitroaniline.

The distances, 6 Å. (α) and 6·5 Å. (β), between the centres of the oxygen atoms in question agree with what is required to explain bands occurring between λ 470 and λ 510. The *quinonoid* formula for erythrohydroxyanthraquinone (XIII) leads to a much smaller

(XIII.)





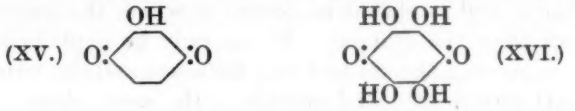
(XIV.)

distance (2·6 or 2·9 Å. according as the 1- and 9-oxygen atoms are on the same or opposite sides of the general plane of the molecule), a distance corresponding to bands between λ 215 and λ 240 in the low ultra-violet region. Meyer and O. Fischer (*Ber.*, 1913, **46**, 85), in the cases of 1-hydroxyanthraquinone and anthrarufin, observed no bands below λ 265, but the lower limit of their investigation was probably not low enough to reach bands situated at λ 220.

The cause of the colour of juglone (5-hydroxy-1 : 4-naphthaquinone, *i.e.*, 1-hydroxy-5 : 8-naphthaquinone) (XIV) and of 1-hydroxyanthraquinone is the same, an orbit round the oxygens attached in positions 1 and 5. The third ring in 1-hydroxyanthraquinone has no effect, as is seen also to be the case by comparison of the bands of naphthazarin with those of alizarin.

It is a curious fact, however, and one not easy to explain, that colour of this height (λ 480 or so) can arise in compounds of only *one* ring, such as hydroxybenzoquinone and tetrahydroxybenzo-

quinone, when examined in alkaline solution. This is nevertheless not strictly analogous, since in juglone the hydroxyl group is



attached, not directly to the quinone ring, but to a carbon atom attached to that ring. Probably a special explanation, similar to that of the high colour of alizarin (see below), is called for here.

The colour of anthrarufin is explained in the same way as that of 1-hydroxyanthraquinone, and the colour of anthraflavin and of *iso*anthraflavin in the same way as that of 2-hydroxyanthraquinone (see p. 1816).

The high colour of alizarin and naphthazarin constitutes part of a general phenomenon seen also in benzeneazopyrocatechol, 3 : 4-dihydroxybenzophenone, etc., whereby the presence of two hydroxol groups adjacent to one another greatly heightens the colour (Table III).

TABLE III.

Substance.	λ.	Comparison substance.	λ.
Benzeneazopyrocatechol ...	480	Benzeneazophenol	433
Phenolpyrocatechol-phthalein	579	Phenolphthalein	554
Pyrocatecholphthalein	652		
o-Hydroxyfluorescein	523+498	Fluorescein	494+457
oo'-Dihydroxyfluorescein ...	550+527		
3 : 3' : 4 : 4'-Tetrahydroxy-benzophenone	449+406	4 : 4'-Dihydroxybenzo-phenone	323

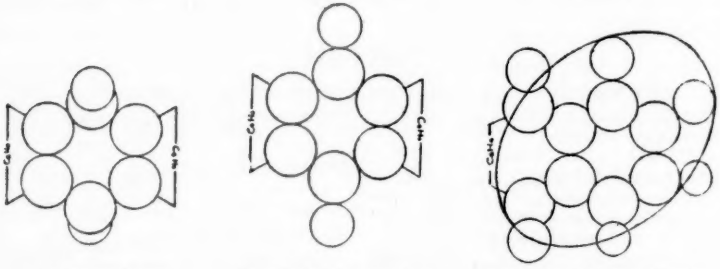
I am of opinion that the explanation is that the electron goes round *both* of the ortho-oxygen atoms as well as the third (distant) oxygen atom (Fig. 5), and thus describes an ovoid orbit which is wider than the normal type of colour ellipse (see J., 1922, **121**, 1810). This connotes a longer path and longer periodic time and higher colour, the eccentricity of the ellipse having been increased. The essential idea in this explanation of the heightening effect of contiguous auxochromes is that the two atoms behave (as in ordinary mechanics) as if their forces were condensed into their "centre of gravity" (the point midway between them), whilst the moving electron has to *touch the outsides* of both of them and so is constrained to move in one plane and thus give an ovoid orbit slightly wider at one end than at the other. In simpler coloured substances, of course, the orbit round two positive centres may be in almost any plane.

The hydroxyanthracenes and the hydroxyanthraquinones having been disposed of, it remains to discuss the colours of the hydroxyanthraquinols and hydroxyanthranols.

(*a*) Anthraquinol itself (in alkali) has a much higher colour than anthraquinone, a phenomenon *sui generis*, since it does not occur in the benzene and naphthalene series, in which the quinol has a lower colour than the quinone. It can only be explained on my theory by supposing the central ring flattened and the two (9 and 10) hydroxyl groups attached outside in the same plane. In this way, the oxygen atoms can be sufficiently separated to agree with the theory and the observed colour (see Table I). In anthraquinone, however, the theory requires that the distance between the oxygen atoms shall be only two-thirds of that required for anthraquinol; this agrees with the ordinary buckled-ring structure. Figs. 3 and 4 represent anthraquinone and alkaline anthraquinol according to the theory.

It is difficult to investigate the hydroxyanthraquinols on account of their great liability to oxidation, but they appear to have even

FIG. 3. FIG. 4. FIG. 5.



Anthraquinone. *Ionised anthraquinol.* *Colour-orbit in alizarin.*

higher colours than anthraquinol, requiring for explanation the ovoid orbit round oxygen atoms situated in the 1 : 9 : 10 and 2 : 9 : 10 positions.

(*b*) The hydroxyanthranols all have much the same colour as anthraquinol, intermediate in "height" between those of the corresponding hydroxyanthracenes and hydroxyanthraquinones. Those of the 1 : 10 and 2 : 10 type have slightly higher colours than those of the 1 : 9 and 2 : 9 type (see Table I). The explanation of their colour on my theory is that the distance between the oxygens is intermediate between that for the hydroxyanthracenes and that for the hydroxyanthraquinones, both of which have been accounted for above.

This shorter distance is accounted for by the fact that the central hydroxyl group of the anthranols is attached in the same way as the *meso*-hydrogen atoms of anthracene. It is thus plain from Fig. 2 that the distance from this hydroxyl to an α- or β-hydroxyl is less than in the case of the hydroxyanthraquinones.

Part II.

Some reference to the views expressed in the Report of the British Association Committee on Spectra and Constitution (1922) is called for from one who still believes that there is a relationship between chemical constitution and the position of absorption bands.

It is, of course, true that the portion of the field of ethereal vibration concerned with colour is less than one five-thousandth of the whole field. The author has, however, shown that the *whole* of the substances chemically related to a single parent substance possessing a band in this minute fraction of the possible field have also a band or bands in this same tiny region (J., 1923, **123**, Tables from p. 2797 to 2803), a fact which if ascribed to coincidence is incredible, but if ascribed to "loading" of the parent substance is eminently reasonable. For example, it appears to be impossible to make any derivative of azobenzene which shall not have a band somewhere between λ 420 and λ 600.

Again, the harmonic results for the anthracene family could be simplified if it is admitted that such of the observations as were made in concentrated sulphuric acid are not directly comparable with those made in alkali. Every such observation should be corrected for the very considerable "loading" effect of the solvent, in the same way as observations in alcohol must be corrected for comparison with observations in water, whereupon the bands coincide.

The case of benzene as studied by McVicker, Marsh, and Stewart is particularly interesting on account of the very definite harmonics arrived at (J., 1923, **123**, 642, 817, 2147). The heads of the Tesla bands were found to be the 33rd, 34th, 35th, 36th, 37th, 38th, and 39th harmonics of a fundamental in the infra-red at $\nu = 987{\cdot}1$ vibrations per cm.* ($\lambda = 10131$ μμ).

The 36th harmonic ($\nu = 35540$, $\lambda = 281\frac{1}{2}$) is the strongest. There is also a fine structure of subsidiary bands, making probably 84 in all between λ 310 and λ 260, all expressible as submultiples of the fundamental (considered as a double band of λλ 10131 and 10162) thus: $\nu = \begin{Bmatrix} 987{\cdot}1 \\ 983{\cdot}6 \end{Bmatrix} \left(1 \pm \frac{n}{216}\right) \times$ harmonics.

Combining this discovery with the knowledge of the positions of two *observed* infra-red bands of benzene at about λλ 1680 and 6750 μμ, we find that we must either assume the real fundamental λ of benzene to be twice that given above (20260 μμ, $\nu = 493{\cdot}5$), in which case the harmonics go up to No. 78; or else keep to the result given above, with no harmonic higher than 39, and explain the band at 6750 μμ by a special hypothesis.

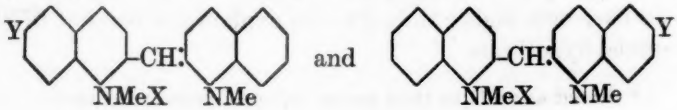
* Stated as 98·71 in their paper, different units being used.

It is fairly clear, however, from the mass of evidence brought forward by Deslandres and referred to later on, that absorption bands possessing a fine structure are caused by the nuclei of the atoms of the molecule and not by the atoms or by the molecule itself.

Part III. Stieglitz's Theory.

Stieglitz, on the contrary, believes with me that there is a connexion between colour and chemical structure or constitution. He has put forward a geometrical theory of the same character as mine (Franklin Institute Centenary Address, 17th September, 1924; *Proc. Amer. Chem. Soc.*, 1920, **43**, 36), but differing fundamentally in that an electron orbit is assumed round *one* atom, but disturbed by the proximity of a second positive centre. The orbit, according to Stieglitz, is not an ellipse round the two positive centres, but is a Cassinian oval round *one* of them, apparently exactly as in Morgan's theory of combination, the electrons being never sufficiently disturbed to become governed by two nuclei (see *Chem. and Industry*, 1924, 1071). A diagram is given there which in my opinion explains the whole subject, not only of chemical combination, but also of absorption and colour. The inner Cassinian ovals (3 in number in Morgan's figure) represent some of the Bohr orbits as disturbed (but not seriously altered) by the proximity of a second positive centre; they represent what happens when electrons are affected by radiation when the second positive centre is distant. The outer ellipse, on the other hand, is the orbit suggested by the present author to explain colour and involves a comparative proximity of two ionised positive nuclei, so that the electron is completely displaced from one and can go round both. An intermediate stage is shown by the permanganate, uranyl, uranous, neodymium, erbium, and praseodymium ions, in which rhythmically related bands occur, but no fine structure in the bands. This is just possibly connected with the intermediate lemniscate orbit.

Stieglitz's theory has not yet had its mathematics worked out and therefore cannot be tested quantitatively against my own, but he produces one case which is inconsistent with my theory (and also inconsistent with the theory of tautomerism), *viz.*, the existence of two distinct dimethylmurexides, one of which is alloxandimethyluramilazomethine and the other dimethylalloxanuramilazomethine. Similarly, on Stieglitz's theory there should be two isomeric forms of every unsymmetrical cyanine, for example,



In Stieglitz's theory, which is founded on the general principle of $\alpha\gamma$-tautomerism, the carbon atom adjoining but outside a double bond is the one round which the perturbed oval orbit is performed by an electron; and the other positive centre is the farthest-away atom of the doubly bonded pair.

Stieglitz's theory gives a better explanation than mine of such problems as the colour of nitrosobenzene, sodium-benzophenone, and other metal-ketyls, and Wieland's substances with bivalent and quadrivalent nitrogen.

Part IV. Deslandres's Theory.

H. Deslandres propounds a law among infra-red absorptions of simple substances whereby they are all connected together, whatever the observed substance may be. He expresses it (*Compt. rend.*, 18 May, 29 June, 17 Aug., and 28 Sept., 1925) in the form $\nu = d_1 q/rs$, in which d_1 is a universal constant or frequency ($1062\frac{1}{2}$ vibrations per cm.), q is the harmonic number of the particular band, r is the number of "octets" in the compound, one being assigned to each hydrogen,* and s is a vulgar fraction (*usually greater than unity*), the value of which is irregular and has not yet been connected with the chemical constitution either of the molecule or of its atoms.

Deslandres's formula can of course be also written: $\lambda = krs/q$, in which q, r, and s are as just defined, but $k = 9412$ $\mu\mu$ when λ is expressed in $\mu\mu$.

Deslandres ascribes the origin of his universal constant to vibration of the α-particle contained in all higher atomic nuclei.

This vibration in the nucleus is supposedly synchronous with the irregular motion of the electron in the ovoid orbit suggested by Morgan (see p. 1820).

I have nevertheless thought it interesting to work out what the values of the vulgar fraction are in the compounds discussed at the beginning of the paper.

In constructing the following table the total variation of the constant has been kept less than $\pm \frac{1}{2}\%$, so as to fix the vulgar fraction. The vulgar fractions resulting are *wholly erratic and disconnected*, and therefore have no real existence.

Benzene gives $\nu = 1066/12 \times 100/9 \times$ (harmonics, *viz.*, 6, 33, 34, 35, 36 ... 39) for the brighter bands and $\nu = 1062\frac{1}{2}/12 \times 100/9 \times$ (harmonics) for the satellites. Here 12 is the value of r; and the vulgar fraction s is 9/100. Henri's vapour-absorption results (*J. Phys. Radium*, 1922, 181) give the fraction as 12/125.

Pyridine gives $\nu = 1066/11 \times 5/3 \times$ (harmonics). Here 11 is the value of r and the vulgar fraction is 3/5.

* *E.g.*, five, not one, in methane: three in water, four in hydrogen sulphide and five in carbon disulphide.

Anthracene gives two alternative results, *viz.*,
(*a*) $\nu = 1066\frac{1}{2}/24 \times 9/8 \times$ (harmonics from 53 to 82), or
(*b*) $\nu = 1060/24 \times 10/3 \times$ (harmonics from 18 to 22); plus
$\nu = 1065{\cdot}3/24 \times 16/5 \times$ (harmonics from 19 to 24).
Naphthalene gives $\nu = 1064/18 \times 14/9 \times$ (harmonics from 34).
Anthraquinone gives $\nu = 1064\frac{1}{2}/24 \times 50/11 \times$ (harmonics from 12).
Dihydroanthracene gives $\nu = 1061/26 \times 35/4 \times$ (harmonics from 7).
Anthranol gives $\nu = 1064\frac{1}{2}/25 \times 29/14 \times$ (harmonics from 29).
1-*Anthrol* gives $\nu = 1067/25 \times 23/15 \times$ (harmonics from 36).
2-*Anthrol* gives $\nu = 1066/25 \times 35/8 \times$ (harmonics from 14).
Anthraquinol gives $\nu = 1066/26 \times 60/17 \times$ (harmonics from 11).
2-*Hydroxy*-9-*anthranol* gives $\nu = 1067/26 \times 16/5 \times$ (harmonics from 16).
3-*Hydroxy*-9-*anthranol* gives $\nu = 1063/26 \times 3/1 \times$ (harmonics from 16).
Naphthazarin gives $\nu = 1064/20 \times 38/15 \times$ (harmonics from 12).
Alizarin gives $\nu = 1060/26 \times 5/3 \times$ (harmonics from 23).
Quinizarin gives $\nu = 1065/26 \times 4/1 \times$ (harmonics from 10).
Anthrarufin gives $\nu = 1064/26 \times 11/9 \times$ (harmonics from 35).
Rufol gives $\nu = 1062\frac{1}{2}/26 \times 11/7 \times$ (harmonics from 36).
Flavol gives $\nu = 1060/26 \times 40/9 \times$ (harmonics from 14).
2 : 7-*Dihydroxyanthracene* gives $\nu = 1065/26 \times 16/11 \times$ (harmonics from 41).
1 : 5-*Dihydroxyanthranol* gives $\nu = 1064\frac{1}{2}/27 \times 32/7 \times$ (harmonics from 13).
2-*Hydroxyanthraquinone* gives $\nu = 1065\frac{1}{2}/25 \times 25/13 \times$ (harmonics from 24).
2 : 6-*Dihydroxynaphthalene* gives $\nu = 1070/20 \times 5/2 \times$ (harmonics from 21).
1-*Hydroxyanthraquinone* gives $\nu = 1066\frac{1}{2}/25 \times 12/5 \times$ (harmonics from 19).

For comparison, Deslandres's results for simple compounds have been recalculated to the same basis, and the vulgar fractions come out quite simple and to some extent interconnected, namely, from $\frac{1}{12}$ to $\frac{1}{2}$.

The inference to be drawn from these considerations is that the absorptions of complex organic substances cannot be correlated with sub-atomic constants in the same way as the absorptions of simple substances.

The absorptions of complex and unsymmetrical substances, whilst no doubt *accompanied* by absorptions due to the valency electrons and the nuclei of the atoms, are therefore essentially molecular. These absorptions arise from the relative positions of the unsaturated atoms in the molecule (N, O, S, along with the group C : C), and will in course of time be fully and quantitatively explained either by Stieglitz's theory or my own.

Deslandres's theory and the harmonic part of the theory given in the British Association Report can be incorporated in mine by supposing that the constant 112 in my equation (connecting λ and molecular distance) is proportional to Deslandres's ratio $10^7 . r/1062\frac{1}{2}q$ (r = number of octets, q = harmonic number when the band is not the fundamental). Deslandres's quantity s is then no

longer a whole number or vulgar fraction, but is a function of a molecular distance of the form $a^{3/2}f(e)$, as given in Part I of this series (J., 1924, **125**, 1137).

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CCXXXVIII.—*Some Observations on the Determination of Surface Tension by Means of Capillary Rise. The Surface Tension of Water, Ethyl Alcohol, Boron Trichloride, and Silicon Tetrachloride.*

By HERBERT MILLS and PERCY LUCOCK ROBINSON.

THE availability of sufficient quantities of boron trichloride and silicon tetrachloride of high purity, together with the absence from the literature of a determination of the surface tension of the former, and the doubtful nature of the value ascribed to the latter, prompted this investigation. To establish the necessary technique, work was begun on water, the value for which has been determined with sufficient frequency to warrant its use for this purpose. Ethyl alcohol was included because of the present uncertainty in the accepted surface tension of this liquid, and also in order to extend certain observations made in the course of the measurements with water.

The capillary-rise method for the determination of surface tension has received considerable attention in recent years, particularly by Richards and Coombs (*J. Amer. Chem. Soc.*, 1915, **37**, 1656, where brief mention is made of previous work), Harkins and Brown (*ibid.*, 1919, **41**, 499), Richards and Carver (*ibid.*, 1921, **43**, 827), and Sugden (J., 1921, **119**, 1483). Study of the literature led at once to a decision to use the important suggestion of Sugden (*loc. cit.*) and Michaelis ("Praktik. d. physikal. Chemie," 1921, 61), *viz.*, that the difference in the capillary rise in two tubes should be used to measure surface tension. This constituted the most convenient method in that it removed at once the difficulty of ascertaining the exact height of the surface of the liquid in the containing vessel, which the elaborate experiments of Richards and Harkins (*loc. cit.*) and their co-workers were designed to overcome. In the present work, however, three instead of two capillary tubes were used, and a vacuum apparatus was devised capable of giving a good fall of liquid surface and of being completely submerged in a thermostat. All measurements were made in an atmosphere consisting solely of the vapour of the liquid in question.

Preliminary work showed that the level of the water in the capillaries fluctuated to an easily measurable extent over a very long period, and furthermore that the movements were not necessarily in the same direction in the three tubes at the same time. All the liquids examined behaved in this way.

Calculation of Surface Tension.

From the general formula relating surface tension to capillary rise, the equation

$$\gamma = r_1 r_2 g(3h + r_2 - r_1)(D - d)/6(r_1 - r_2)$$

may be derived, where r_1 and r_2 are the radii of two capillaries, h is the observed difference in height of two meniscuses in these tubes, D and d are, respectively, the densities of the liquid and the atmosphere over it, and g is the acceleration due to gravity. The value of g used was 981·45, and the surface tension, γ, is expressed in dynes per cm. In this investigation the capillaries were narrow enough to avoid any serious departure of the meniscuses from a hemispherical form, thus rendering unnecessary the corrections suggested by Sugden (*loc. cit.*). The diameters of tubes available were such that the rises in two were to nearly the same height, while that in the third was much lower, and as the proportional error in the measurements of h tends to increase as h diminishes, the smallest difference was not used in the calculation of surface tension.

EXPERIMENTAL.

The Preparation and Calibration of the Capillary Tubes.—The importance of a very rigorous cleaning of the capillary tubes cannot be overestimated : Harkins and Brown (*loc. cit.*), who gave this matter particular consideration, used prolonged passage of the vapour of the liquid concerned in the determination as the final cleaning process before use. The tubes here employed were steeped for several days in a solution of chromic acid in concentrated nitric acid, washed well by drawing water through them, almost submerged for 3 hours in boiling alcohol in such a manner that there was a continuous regular flow of liquid up through them, and finally steamed for 3 hours in the apparatus shown in Fig. 1—A is the capillary under treatment, B the jacket surrounding it, and C a tube of special form delivering steam under pressure from the purest distilled water. For the determinations with water the tubes were put into the apparatus wet from the steaming, but for the other determinations they were drained by holding them in a vertical position and touching the lower end with clean filter paper, and then dried at 110° in an electrically heated oven. After

their introduction into boiling alcohol the capillaries were handled only with several layers of clean filter paper between the fingers and the glass, in order entirely to prevent the possibility of the formation of a grease film.

The calibration of the capillary tubes was effected by three different methods in the case of A, B, and C, using (1) an ordinary physical travelling microscope, (2) a cathetometer, and (3) a travelling microscope, made by the Cambridge Instrument Company, and reading directly to 0·01 mm. and by estimation to 0·002 mm. The last instrument only was used in the case of D, E, and F. The mercury threads employed were weighed, after being removed from the tubes by means of dry air to a small glass weighing-bottle lid, on a special balance with calibrated weights, with the precautions usually taken in precise work. The weighings were to 0·01 mg. The uniformity of the bore was first examined by the introduction of a short thread of pure mercury, the length of which was accurately measured, in overlapping positions, along the whole length to be used. The results obtained by using the Cambridge instrument are in Table I, where the lengths of the threads are given in mm., and the figures marked with an asterisk denote the distance of the middle of the threads from the lower ends of the tubes.

FIG. 1.

FIG. 2.

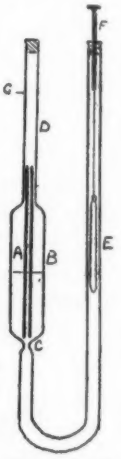

FIG. 3.

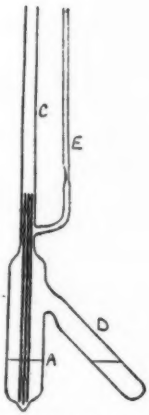

TABLE I.

A.		B.		C.	
8 cm.*	8·235	7 cm.*	10·980	8 cm.*	11·397
	8·246		10·991		11·391
	8·233	2 cm.*	10·991		11·395
	8·238				11·394
2 cm.*	8·247				11·399
				2 cm.*	11·396

D.		E.		F.	
8 cm.*	13·498	5 cm.*	14·757	4 cm.*	13·173
	13·478		14·767		13·174
	13·477		14·760	2 cm.*	13·164
2·5 cm.*	13·489	1 cm.*	14·757		

The uniformity of the tubes may be expressed as a maximum percentage difference in the length of the threads; the following results are obtained: A, 0·17%; B, 0·09%; C, 0·07%; D, 0·09%; E, 0·08%; F, 0·08%. These tubes compare unfavourably with those of Richards and Coombs (*loc. cit.*), for which uniformity was claimed, and also with those of Harkins and Brown (*loc. cit.*), where the difference was 0·03% on a thread of about 16·8 mm. in length, but they were the best from 50 lb. of capillary tubing, much of it specially drawn for this research, and their selection involved 4 weeks of constant work. The radii were obtained by measuring and weighing three threads about 4 cm. long and one or more shorter threads of pure mercury about 1 cm. long in each tube, the temperature at the time of measurement being noted and the density of the metal being computed (Smithsonian Physical Tables, 7th Edtn.). The observation of Harkins and Brown (*loc. cit.*) that there is a definite sag in the mercury meniscus with the tubes in a horizontal position even when the radius is as small as 0·2 mm. was confirmed; it was corrected for, as suggested by them, by subtracting the length and weights respectively of a shorter thread. The radii of the tubes were determined with the Cambridge measuring microscope, the calibrations being restricted to the lengths actually used, and are believed to have an accuracy of 0·1% and 0·05% for the narrower and the wider tubes respectively.

TABLE II.

Tube	A.	B.	C.	D.	E.	F.
r (in mm.)	0·07325	0·20168	0·25287	0·27165	0·41354	0·49920

The ends of all tubes were examined for ellipticity with a microscope and found to be satisfactory in this respect.

The Surface Tension of Water.—Preliminary work with three capillary tubes of approximately the bore indicated above showed that definite vertical movement of the meniscuses took place with the tubes either arranged in a triangular formation 4 cm. apart or bound together in a bundle. The results indicated that concordant surface tensions would be obtained from either arrangement provided that sufficient time was allowed to elapse after lowering the level of the liquid. This led to the construction of a vessel of the form indicated in Fig. 2, in which A represents the prepared capillaries, held in position in the wider tube, B, by the taper at C and the extension, D. The fall in level of the liquid was secured by raising the glass plunger, E, which was suspended from the long screw, F. This apparatus, charged with first-quality water, was submerged to the point G in a thermostat at 25° ± 0·01°, and the height of the water in the capillaries was observed by

means of a cathetometer reading to 0·01 mm. at intervals of about 10 minutes for 2·5 hours from the time at which the level of the liquid was lowered. During this period the heights of the menisci in the three tubes fell irregularly, giving, when plotted against time, a sinuous downward-sloping curve, recording maximum falls of 0·72 mm., 0·64 mm., and 0·74 mm., respectively. As the upper part of the apparatus, which was closed with a loosely fitting cork, had protruded from the bath, the fall was ascribed, correctly as it was subsequently proved, to evaporation. This explanation was tested by maintaining the bath at 17·4°, *i.e.*, about 0·5° below laboratory temperature, and repeating the observations without changing the water or re-treating the tubes; 24 observations, spread uniformly over 5 hours, were taken, with the result that sinuous, slightly rising curves were now obtained, showing minimum points 0·12, 0·17, and 0·17 mm., respectively, below the initial heights after about 2·5 hours, and a maximum rise at the end of the period of 0·39, 0·22, and 0·04 mm. above. Such changes could not be explained by either evaporation or irregular drainage, and further investigation was undertaken in an apparatus (Fig. 3) which consisted of a barrel, A, 2·5 cm. wide, terminated below in a cone-shaped point and above in the centrally disposed tube, C, suitable in width for holding steadily the three capillary tubes. The side limb, D, was provided for lowering the level of the liquid, and E with its capillary served for filling and evacuation. This vessel was cleaned with chromic–nitric acid mixture, well washed with distilled water, maintained full of boiling alcohol for 4 hours, and finally well rewashed with best-quality water. When thus prepared, the freshly steamed capillary tubes were slid down C into such a position that the three could be observed from the selected direction, and C was drawn off just above the tops of the capillaries. Water (prepared by treating first-quality distilled water with a trace of alkaline permanganate, redistilling with considerable rejection of head and tail fractions, and again twice distilling the main fraction with rejections) was used for the three final washes in the apparatus. These distillations were carried out successively without delay, and the final material, which was distilled directly into E, served as the sample to be examined. E was at once attached to the pump and the whole of the air was removed, the water being warmed to facilitate this, after which the apparatus was sealed off under the pressure of water vapour only. The surface-tension vessel was completely submerged in a thermostat maintained within $\pm$ 0·01° of the required temperature and, a fall in level of the liquid having been obtained by tilting the apparatus and allowing a portion to run into D, the heights

of the meniscuses were observed with a cathetometer reading to 0·01 mm. The tubes were arranged so that the threads of all could be observed without swinging the telescope of the instrument in a horizontal plane, both they and the cathetometer having been brought to a vertical position. The glass forming the barrel, A, had been carefully selected for uniformity and lack of distortion, and careful measurements, made at different places over the range actually used, indicated that the images of the meniscuses were not appreciably changed in apparent relative position. The regularity of the results derived from different sets of observations bears out this conclusion. Table III gives one complete set (Set K) of observations for water at 25° and indicates the general nature of the fluctuations in height observed throughout this work, namely, that the most rapid and extreme variations are found within the first hour, that these variations grow less with time, and that after a period of about 10 hours they have almost entirely vanished. Table IV gives the surface tension calculated from the data in Table III, and shows that the two values come closer together with the passage of time, the difference falling from 0·26 to 0·07 unit.

TABLE III.

Time from zero (min.) ...	6	18	34	50	86	123	158	219	271	340
Tube F (mm.)	0·62	0·77	0·71	0·69	0·72	0·75	0·75	0·78	0·78	0·78
Tube D (mm.)	25·56	25·41	25·49	25·46	25·48	25·49	25·52	25·53	25·56	25·55
Tube C (mm.)	29·59	29·60	29·63	29·65	29·60	29·62	29·67	29·66	29·66	29·71

Time from zero (min.) ...	389	458	520	575	636	696	754	787	813
Tube F (mm.)	0·85	0·77	0·84	0·83	0·83	0·83	0·83	0·83	0·83
Tube D (mm.)	25·55	25·56	25·58	25·60	25·63	25·64	25·64	25·64	25·64
Tube C (mm.)	29·70	29·70	29·72	29·69	29·70	29·71	29·70	29·71	29·70

TABLE IV.

	First hour.		Middle hour.		Last hour.	
Tubes.	Mean h (mm.).	γ.	Mean h (mm.).	γ.	Mean h (mm.).	γ.
C and F	28·920	72·31	28·900	72·26	28·875	72·20
D and F	24·783	72·05	24·770	72·01	24·810	72·13

TABLE V.

Set.	Temp.	Time range (hrs.).	Tubes.	h.	γ.	γ, mean.
I.	25°	11·5	C, F	28·86	72·16	72·16
J.	21	7	C, F	29·07	72·75	72·75
K.	25	14	C, F	28·88	72·20	72·17
			D, F	24·81	72·13	

Table V summarises the data for water using $(D - d)_{25°} = 0{\cdot}99705$ and $(D - d)_{21°} = 0{\cdot}99800$. In Sets I and J only one result is recorded because of the behaviour of tube E, which, although free from irregularity of bore or defect obvious under the microscope,

persisted in preventing water from rising beyond a certain point. Presumably this was due to some condition of the surface of the glass at this point which tended to inhibit wetting.

The Surface Tension of Alcohol.—A vessel similar to that described in the case of water was successively cleaned with chromic–nitric acid mixture, alkali, water, alcohol, and ether, and finally dried along with the capillary tubes, which had been treated as described previously, in an electrically heated oven. The alcohol used in Sets D and E was only roughly dried, that used in Set F was dried rather more thoroughly but still probably contained traces of moisture. Special precautions were, however, taken in the preparation of the alcohol for Set H, which was absolute alcohol redistilled with considerable rejections, refluxed over lime warm from burning for 3·5 days, the lime being changed at the end of the first day and a head and a tail fraction being rejected in the process. In distilling the liquid into the dried-out vessel, special precautions were taken to avoid contact with the air as far as possible; the whole operation lasted less than 0·25 hour and the apparatus was at once evacuated and sealed off. Table VI summarises the results for alcohol, all but Set H being considered as preliminary work with material containing water. The values $(D - d)_{25°} = 0{\cdot}78491$ and $(D - d)_{15°} = 0{\cdot}79352$ were used throughout.

TABLE VI.

Set.	Temp.	Time range (hrs.).	Tubes.	h.	γ.	γ, mean.	Remarks.
C.	25°	4·0	A, B	49·81	22·04	22·06	Alcohol containing moisture.
			A, D	57·12	22·09		
E.	15	7·0	A, B	51·33	22·96	22·96	
			A, D	58·86	22·96		
F.	25	12	A, B	49·01	21·70	21·69	Drier alcohol.
			A, D	56·19	21·68		
H.	25	24	A, B	48·77	21·58	21·59	Dry alcohol.
			A, D	55·97	21·60		

The Surface Tension of Boron Trichloride.—Boron trichloride of high purity (for history of material and manipulation see subsequent paper by Parker and Robinson) was distilled into a similar surface-tension apparatus which had been thoroughly cleaned, dried, and evacuated. Two sets of observations were taken—at 25° with 15 readings, and at 21° with 10 readings. The data are given in Table VII, the values $(D - d)_{25°} = 1{\cdot}3144$ and $(D - d)_{21°} = 1{\cdot}3207$ being used.

The Surface Tension of Silicon Tetrachloride.—The procedure was exactly as with boron trichloride (for history of material and manipulation see Parker and Robinson, *loc. cit.*), but, unfortunately,

TABLE VII.

Set.	Temp.	Time range (hrs.).	Tubes.	h.	γ.	γ, mean.
M.	25°	10	A, B	21·71	16·07	16·07
			A, D	24·91	16·07	
N.	21	9·5	A, B	22·22	16·52	16·52
			A, D	25·49	16·52	

at the end of the distillations the sudden boiling of a drop or two of liquid in the plunger arm of the special joint caused a fracture, and air entered the apparatus. The broken portion was at once drawn off and the apparatus attached to the pump and evacuated so that exposure to air was not longer than 1·5 minutes. There was no evidence of hydrolysis in the apparatus, nor did the behaviour of the liquids in the capillaries suggest that the admission of air had had any detrimental effect; nevertheless, these results are given provisionally and it is proposed to repeat this portion of the work with other material of similar purity which is available. Table VIII gives these provisional results, 15 observations being taken in each set; $(D - d)_{25°} = 1{\cdot}4685$ and $(D - d)_{21°} = 1{\cdot}4771$ were used.

TABLE VIII.

Set.	Temp.	Time range (hrs.).	Tubes.	h.	γ.	γ, mean.
O.	25°	12	A, B	23·11	19·11	19·11
			A, D	26·51	19·11	
P.	21	12	A, B	23·54	19·58	19·59
			A, D	27·01	19·59	

Discussion.

It has been shown that tubes of a much smaller bore than have usually been employed can be used in the determination of surface tension to a high degree of accuracy by the method suggested by Sugden (*loc. cit.*), but concordant results with two or more such tubes are obtained only several hours after the lowering of the liquid level. The thorough cleaning of the capillaries emphasised by other workers is found to be necessary. Distinct advantage attends the use of three in place of two tubes, and the results are the same whether they be separated from one another by several cm. or bound together in a bundle, the latter arrangement being more convenient. During the first hour or so, the meniscuses in the capillary tubes show slow oscillations, sometimes opposite in direction in two tubes at the same time, or coinciding with no movement in another tube, while the mean heights tend to decrease throughout the same period, and surface tensions calculated from differences in the heights obtained at any moment do not show

good agreement amongst themselves. These movements gradually decrease and are followed by a series of more or less spasmodic rises which continue, although they may be separated by intervals as long as one or two hours, until the maximum rise for each tube is reached. That these rises are to be ascribed to surface forces, and not to any change in level of the main liquid surface from drainage or other causes, is proved by the fact that they are invariably preceded by a greatly increased curvature of the meniscus, as though the centre were being drawn down, whilst, furthermore, the movements take place at times and to extents which are not the same in the different tubes.

If the forces producing the rises were being applied at the base of the columns, a flattening of the meniscuses and concurrent rises in the three tubes would be anticipated. The whole subject is being investigated, but a careful examination of the available data leads to the conclusion that for the same liquids the changes in the heights of the meniscuses decrease with increasing size of capillary, while the period required to reach the maximum rise and the equilibrium is slightly less in the wider tubes, and that with the same bore the magnitude of these changes in the liquids considered grows less in the order alcohol, water, silicon tetrachloride, boron trichloride. The inference made here is that, after the oscillations of the initial period have damped down, the change in level of the meniscus due to spasmodic rises is probably related to viscosity, for the viscosities of alcohol and water are known to decrease in the order noted, while those of the chlorides, although apparently not determined, are certainly less than that of water. It is suggested that the maximum rise attained when the meniscuses are at rest corresponds to the true static equilibrium between surface energy and gravity, and that the figure calculated from h in these conditions corresponds to the true surface tension. It should be pointed out that, once equilibrium is reached, the meniscuses are not observed to move either of their own accord or when the vessel has been made to tremble by tapping, thus suggesting the stability above implied.

Surface tensions are usually given at 20°, and Table IX records the values now found (in contact with only the vapour of the substance) corrected to this temperature, together with the change per degree.

TABLE IX.

Substance.	γ.	Change in γ per degree.
Water	72·90 ± 0·04	0·15
Alcohol	22·05 ± 0·01	0·09
Boron trichloride	16·70 ± 0·01	0·11
Silicon tetrachloride	19·71 ± 0·01	0·12

The value for water agrees most closely with the 72·80 of Harkins and Brown (*loc. cit.*), but is much higher than the 72·74 of Richards and Coombs (*loc. cit.*), the 72·70 of Sugden (*loc. cit.*), the 72·61 of Worley (J., 1914, **105**, 266), or the 72·8 given as the most probable value by Freundlich ("Colloid and Capillary Chemistry," 1927, 24). In the case of alcohol there have been numerous previous determinations yielding results varying from 21·2 to 22·4. The value given above agrees closely with the 22·0 of Ramsay and Shields (*Phil. Trans.*, 1893, **184**, 647), and the precautions taken in this work render it the most probable value at the present time. The surface tension of boron trichloride has not hitherto been recorded. Silicon tetrachloride has received attention from Ramsay and Shields (*loc. cit.*), who found $\gamma = 16{\cdot}31$ at 18·9°, *i.e.*, 16·20 at 20°; from Walden (*Z. anorg. Chem.*, 1900, **25**, 218), who found $\gamma = 18{\cdot}20\ (1 - 0{\cdot}00548t)$, *i.e.*, 16·23 at 20°; and from Mendeléev (*Pogg. Ann.*, 1870, **141**, 618), who found 15·13 at the b. p. (57°), which is approximately equivalent to 19·20 at 20°.

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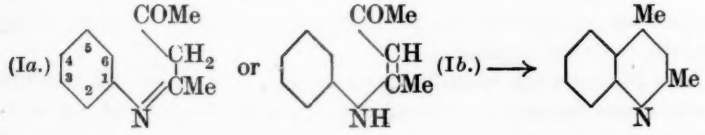
CCXXXIX.—*The Factors controlling the Formation of Some Derivatives of Quinoline, and a New Aspect of the Problem of Substitution in the Quinoline Series.*

By ELWYN ROBERTS and EUSTACE EBENEZER TURNER.

AN apparently excellent method for obtaining quinoline derivatives (II) is that devised by Combes (*Bull. Soc. chim.*, 1888, **49**, 90; *Compt. rend.*, 1887, **106**, 142), namely that of warming, with concentrated sulphuric acid, the condensation products (I*a* or I*b*) of acetylacetone with primary aromatic amines:



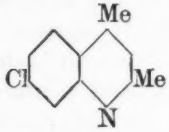
Previous work has shown that most simple substituted anilines condense readily with acetylacetone, even where, as in 2 : 6-dimethoxyaniline, a marked steric effect must be supposed to occur (Turner, J., 1917, **111**, 1), and it has now been found that, although *o*-, *m*-, and *p*-chloro-, 2 : 4-, 3 : 4-, and 3 : 5-dichloro-aniline do so, 2 : 5-dichloroaniline condenses only partially. The ease of condens-

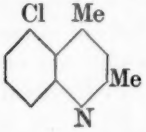
ation appears to be affected most by the basicity of the aniline used, for no nitroaniline, simple or complex, can be caused to condense with acetylacetone. It may be noted that acetylacetone condenses less well with most bases than does, for example, salicylaldehyde, which rapidly converts 2 : 5-dichloroaniline into the o-*hydroxybenzylidene* derivative.

The second stage of the Combes quinoline synthesis, namely, the intramolecular condensation of an anil of acetylacetone, is, however, much more definitely affected by the nature of the substituents present. Thus, whilst the condensation products, with acetylacetone, of aniline and *p*-toluidine (Combes, *loc. cit.*), those of 2 : 3-, 2 : 5-, and 3 : 4-dimethoxyaniline, that of 2-bromo-4 : 5-dimethoxyaniline (Lions, Perkin, and Robinson, J., 1925, **127**, 1158), and, as now shown, that of *m*-chloroaniline readily pass into the corresponding substituted 2 : 4-dimethylquinolines, a number of not very dissimilar anils do not, under corresponding conditions, undergo conversion into quinolines to any measurable extent. Into this second class fall the condensation *products*, with acetylacetone, now examined for the first time, of *o*- and *p*-chloroanilines, 2 : 4-, 2 : 5-, and 3 : 5-dichloroanilines, and *o*-anisidine. Koenigs and Mengel (*Ber.*, 1904, **37**, 1322) were similarly unable to obtain 6-methoxy-2 : 4-dimethylquinoline from β-*p*-methoxyanilinopropenyl methyl ketone. Marckwald and Schmidt (*Annalen*, 1893, **274**, 331) showed that, whilst both *m*- and *p*-phenylenediamines condensed with two molecules of acetylacetone, treatment of the products with concentrated sulphuric acid afforded an amino-2 : 4-dimethylquinoline (and not a phenanthroline) in the former case, and no quinoline at all in the second. Incidentally, Bülow and Issler (*Ber.*, 1903, **36**, 4013) effected the conversion of β-*m*-hydroxyanilinopropenyl methyl ketone into a mixture of hydroxy-2 : 4-dimethylquinolines by using, not concentrated sulphuric acid, but hydrogen chloride and glacial acetic acid as the condensing medium.

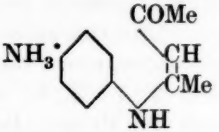
It appears possible to draw certain definite conclusions from these facts. For example, when a strongly ortho-para directing group is present in the meta-position to the nitrogen atom [3 or 5 in (I)], condensation proceeds readily, even if a similar group is present in an unfavourable position, as in 2 : 5-, 3 : 4-, and 2 : 3-dimethoxyaniline. On the other hand, a strongly ortho-para directing group present in position 4 (I), in absence of other substituents in favourable positions, appears to be sufficient to prevent quinoline formation (*o*- and *p*-anisidine). The effect of chlorine is what would be anticipated from our knowledge of its power as a directive influence. Thus, whilst one chlorine atom in a favourable

position (meta to the nitrogen atom) is associated with exceptional ease of quinoline formation, a chlorine atom in another position prevents condensation (but compare the case of 3 : 4-dichloroaniline, below). It therefore seems that in these cases the ortho-directive influence of the nitrogen atom is, extraordinary though it may appear, feebler than the opposing ortho-para influence of a chlorine atom. Further, whilst steric factors do not prevent the operation of the directive influence of a methoxyl group, they appear to more than neutralise that of even two chlorine atoms. Thus, β-3 : 5-dichloroanilinopropenyl methyl ketone [chlorine in positions 3 and 5 in (I)] cannot be converted into the corresponding quinoline, although the two chlorine atoms and the nitrogen atom would be expected to favour condensation. From this fact, one might deduce that the dimethylquinoline formed from *m*-chloroaniline would be (III) rather than (IV), since the steric effect would operate against the formation of the latter. That this inference is correct is proved

(III.) 



(IV.)



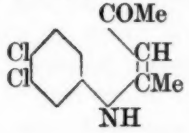
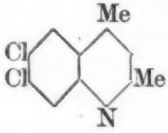
(V.)

later. It would also appear to follow from this that the compound obtained by Marckwald and Schmidt (*loc. cit.*) from *m*-phenylenediamine is 7-amino-2 : 4-dimethylquinoline. The non-formation of a quinoline from *p*-phenylenediamine is of interest, for, since β-*p*-aminoanilinopropenyl methyl ketone is presumably present as the ion (V) in concentrated sulphuric acid solution, the most favoured position would appear to be that where condensation could occur, but does not.

It is somewhat difficult, on the other hand, to explain why β-*p*-toluidinopropenyl methyl ketone [methyl in position 4 in (I)] is quantitatively converted into 2 : 4 : 6-trimethylquinoline (see Experimental). For, since *p*-chlorotoluene nitrates to roughly equal extents in the 2- and 3-positions (Holleman, *Rec. trav. chim.*, 1909, **28**, 408), the influence of a methyl group should approximate to that of a chlorine atom in type (I). The explanation may be, however, that just as replacement by chlorine, but not by methyl, diminishes the basicity of the aniline molecule, so it diminishes the ortho-para directive influence, already small, of the nitrogen atom in the acetylacetone anils.

Particular interest attaches to the action of sulphuric acid upon the condensation product of acetylacetone with 3 : 4-dichloroaniline (VI). Preliminary experiments showed no condensation, but then, on one occasion, a good conversion into a dichlorodimethylquinoline,

m. p. 119—120°, occurred. Attempted repetition of the successful experiment on at least a dozen occasions never gave an isolable quantity of this product, which, however, has been shown to be 6 : 7-*dichloro*-2 : 4-*dimethylquinoline* (VII).

(VI.)  (VII.) 

We regard these results as indicating that in (VI) there is a very delicate balance between the antagonistic and the favourable influences, so that the slightest variation from the ideal conditions for condensation is sufficient to prevent ring closure.

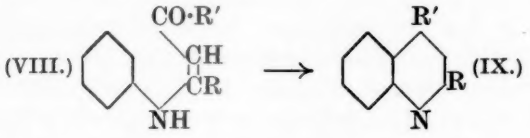
The non-formation of quinoline in the cases referred to above can hardly be due to an initial condensation to the extent of a few units %, the water formed then, with the sulphuric acid, hydrolysing the unchanged anil of a weak base, for if this were so, condensation should have been observed where absolute or slightly fuming sulphuric acid was used.

Partly in order to prove the constitution of the products (III) and (VII), and partly to institute a comparison of the Combes condensation with others leading to the same, and other, quinolines, we next directed our attention to the method first used by Reed (*J. pr. Chem.*, 1885, **32**, 630), but generally known as the Beyer condensation (*ibid.*, 1886, **33**, 393). When heated with a suitably aged mixture of paraldehyde, acetone, and hydrogen chloride at 100° in presence of nitrobenzene, *o*-, *m*-, and *p*-chloro-, 2 : 4-, 2 : 5-, 3 : 4-, and 3 : 5-dichloro-, and 2 : 4 : 5-trichloro-aniline were converted into dimethylquinolines, although in every case the yield was poor. On the other hand, *m*-nitroaniline was apparently unaffected, whilst *o*-nitroaniline was converted in good yield into a *compound* other than the expected 8-nitro-2 : 4-dimethylquinoline. Again, 3-chloro-6-nitro- and 3 : 4-dichloro-6-nitro-aniline were converted into tarry substances from which nothing could be isolated. The object of attempting the latter two condensations was to synthesise reference compounds needed for the elucidation of the structure of (III) and (VII).

When on one occasion 3 : 5-dichloroaniline was heated with a paraldehyde–acetone–hydrogen chloride mixture prepared 2 months previously, no 5 : 7-dichloro-2 : 4-dimethylquinoline was obtained, but, in good yield, a *substance* which has not yet been identified.

The above results become of even greater interest when the Combes and the Beyer condensation are compared with those of Doebner and von Miller and of Skraup. The last three of these

condensations have been the subject of repeated investigation, but much uncertainty still exists as to the precise mechanism underlying them. Consideration of the papers of von Miller (*Ber.*, 1891, **24**, 1720; 1892, **25**, 2072), Jones and his collaborators (J., 1910, **97**, 632; 1911, **99**, 334; 1912, **101**, 1376), Blaise and Maire (*Compt. rend.*, 1907, **144**, 93; *Bull. Soc. chim.*, 1908, **3**, 658), and Simon (*Compt. rend.*, 1907, **144**, 138) suggests, however, that the four reactions under discussion are similar in one respect, namely, that in the last stage they all appear to conform to the general scheme of (VIII) passing into (IX):



The Skraup, Doebner–Miller, Beyer, and Combes condensations are represented by this scheme when R = R′ = H, R = Me and R′ = H, R = R′ = Me, and R = R′ = Me, respectively. The assumption is not invalidated by the observations of Knoevenagel and his collaborators (*Ber.*, 1922, **55**, 1923; 1923, **56**, 2414), nor can the fact that the so-called "aldol bases" are formed in the Doebner–Miller reaction be regarded as involving a conception essentially different from that represented by the above scheme.

Decker and Remfry (*Ber.*, 1905, **38**, 2773) concluded that both the Skraup and the Doebner–Miller reaction converted mono-meta-substituted anilines into 5-substituted quinolines. A closer examination of the facts, however, shows that this is hardly the case, since Skraup reactions with these compounds actually fall into two classes. Those in which the meta-substituent is meta-directing (NO_2, SO_3H, and CO_2H) give almost entirely 5-substituted quinolines (La Coste, *Ber.*, 1883, **16**, 669; Claus and Stiebel, *Ber.*, 1887, **20**, 3095; Knueppel, *Ber.*, 1896, **29**, 703; Decker, *J. pr. Chem.*, 1901, **63**, 573; **64**, 85; Lellmann and Lange, *Ber.*, 1887, **20**, 1446; Schlossen and Skraup, *Monatsh.*, 1881, **2**, 518; Skraup, *Ber.*, 1882, **15**, 893; Skraup and Bronner, *Monatsh.*, 1886, **7**, 139, 519; Lellmann and Alt, *Annalen*, 1887, **237**, 307), whilst, when the meta-substituent is ortho-para directing (Cl, Br, Me, OH), either a mixture of 5- and 7-derivatives results, or almost exclusively the 7-derivative (La Coste and Bodewig, *Ber.*, 1884, **17**, 926; La Coste, *Ber.*, 1885, **18**, 2940; Claus and Tornier, *Ber.*, 1887, **20**, 2872; Claus and Vis, *J. pr. Chem.*, 1889, **40**, 382; Skraup, *Monatsh.*, 1882, **3**, 381, 531; Skraup, *loc. cit.*; Skraup and Bronner, *loc. cit.*; von Braun, Gmelin, and Schultheiss, *Ber.*, 1923, **56**, 1341). On the other hand, *m*-

nitroaniline gives mainly 5-nitroquinaldine (Decker and Remfry, *loc. cit.*), whilst it does not condense to any observable extent under the conditions of the Beyer synthesis.

m-Chloroaniline gives rise to a mixture of 5- and 7-derivatives in the Skraup reaction (La Coste, 1885, *loc. cit.*; Claus and co-workers, *J. pr. Chem.*, 1893, **48**, 253, 270), mainly to the 7-derivative in the Beyer reaction, and to the 7-derivative only in the Combes condensation. An inspection of (VIII) and (IX) suggests that the difference in position of condensation in the three reactions mentioned is due to the steric effect of R′. Possibly the same effect prevents the formation of 5-nitro-2 : 4-dimethylquinoline by the Beyer process, since for some reason, not clear at present, the quinoline ring apparently prefers to form in the ortho-position with respect to a nitro-group rather than in the para-position. This point is of considerable interest, since in the nitration of nitrobenzene, more ortho- than para-substitution occurs.

Which constitution (I*a* or I*b*) more accurately represents the constitution of the condensation products of acetylacetone with anilines cannot now be discussed, but we have observed that dibenzoylmethane condenses with freshly distilled aniline to give, as one product, a compound identical with that obtained by Watson (J., 1903, **83**, 1326) by the addition of aniline to benzoylphenylacetylene, CPh:C·COPh. Watson regarded his compound as being either CHPh:C(NHPh)·COPh or NHPh·CPh:CH·COPh, and the formation of the same compound from dibenzoylmethane shows that the latter reacts in the enolic form, to give the second of the two substances formulated, *i.e.*, to give the anilino-derivative and not the phenylimino-compound, COPh·CH_2·CPh:NPh. One of us has previously observed (Turner, *loc. cit.*) that when acetylacetone is heated with excess of aniline it undergoes scission, giving acetanilide. We have now found that benzanilide is formed as a second product when aniline reacts with dibenzoylmethane.

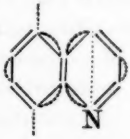
The factors governing substitution in quinoline compounds are apparently less complex than would be assumed from first considerations. Quinoline and 2-methylquinoline both nitrate simultaneously in the 5- and 8-positions (Claus and Kramer, *Ber.*, 1885, **18**, 1243, etc.), whilst 4-methylquinoline, on the other hand (Busch and Königs, *Ber.*, 1890, **23**, 2687), gives only the 8-nitro-derivative, an effect almost certainly due to the steric influence of the methyl group in position 4. 2 : 4-Dimethylquinoline would therefore also be expected to nitrate in position 8, and has actually been found to do so. The *nitro*-compound on reduction gives 8-*amino*-2 : 4-*dimethylquinoline*, and the latter is converted by the Gattermann diazo-method into 8-*chloro*-2 : 4-*dimethylquinoline*,

identical with the product of the Beyer condensation, using *o*-chloroaniline.

It would be thought that most of the substitution reactions of quinoline could be referred to the presence of the nitrogen atom, but actually this is not the case. Nor is it quite clear by what process conditions of nitration affect the proportion of 5- and 8-substitution in quinoline itself. For example, when quinoline nitrate is added to fuming sulphuric acid, 5-nitroquinoline results (Dufton, J., 1892, **61**, 783), whilst mixed acid converts quinoline itself mainly into the 8-isomeride (Königs, *Ber.*, 1879, **12**, 449). If the former nitration were explained as that of the ion (X), and the latter as that of the free base, then it would be difficult to explain why *iso*-

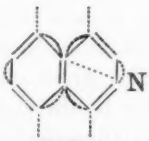
(X.)

(XI.)

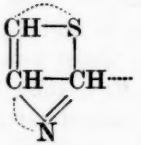
(XII.) 

quinoline does not nitrate in position 7 (Claus and Hoffmann, *J. pr. Chem.*, 1893, **47**, 253), and even more so why quinolinium methonitrate also nitrates in positions 5 and 8 (Decker, *Ber.*, 1905, **38**, 1274). A comparison of quinoline and naphthalene appears to solve these difficulties, for, just as the behaviour of naphthalene is tolerably well explained by Thiele's formula (XI), so that of quinoline should be explained, at least to a considerable extent, by (XII), the following two facts being borne in mind: (1) Mills and Smith (J., 1922, **121**, 2724) concluded that in the naphthalene molecule the two central (*i.e.*, un-numbered) carbon atoms are joined by a double bond, (2) the pyridine molecule is markedly non-reactive, a property capable of explanation by formulating it as (XIII), since the highly unsaturated nitrogen atom may be assumed to take up residual affinity from the 4-position. That is, one would expect to find reactivity in the 5- and 8-positions in quinoline, corresponding to the reactivity of the *four* α-positions in naphthalene.

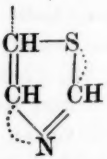
(XIII.)



(XIV.)



(XV.)



(XVI.)

Indeed, the application of similar reasoning to the *iso*quinoline and thiazole molecules suggests an alternative explanation of the interesting results obtained by Mills and Smith (*loc. cit.*), *viz.*, in

*iso*quinoline, chlorine * should be more reactive (towards hydriodic acid and red phosphorus) in position 1 than in position 3, and in thiazole, since the nitrogen atom is less saturated than the sulphur atom (compare XV and XVI), reactivity should be associated more with position 2 than with position 4—which is actually the case. If this explanation is correct, reactivity should also be greater in position 5 than in position 4.

If (XIV) accurately represents the *iso*quinoline molecule, the known nitro-derivative might be expected to be the 5- rather than the 8-compound.

Quinoline actually resembles naphthalene very strongly in its substitution reactions, since α-nitronaphthalene corresponds with either 5- or 8-nitroquinoline. The analogy becomes even more striking when it is realised that, just as naphthalene-α-sulphonic acid is converted by concentrated sulphuric acid under definite conditions into the β-isomeride, so quinoline-5-sulphonic acid is converted by the same reagent at 250—300° into the 6-isomeride (Lellmann and Reusch, *Ber.*, 1889, **22**, 1391).

Nitration of 6-, 7-, and 8-chloro-2 : 4-dimethylquinoline appears to be controlled almost entirely by 5 : 8 reactivity, and by the ortho-para directive influence of the chlorine atom, which can act partly in the same sense. These overcome the steric effects which must be assumed in the case of the 6- and the 7-chloro-compound [compare the nitration, by Armstrong and Wynne, of β-chloronaphthalene, where the α-position *could* be avoided, and is (*Chem. News*, 1889, **59**, 225)]. For example, 6-chloro- and 7-chloro-2 : 4-dimethylquinoline nitrate in positions 5 and 8, respectively. The 8-chloro-compound nitrates in position 5, as is shown by the fact that the *nitro*-compound, on reduction, affords an *amino*-compound which is convertible into 5 : 8-*dichloro*-2 : 4-*dimethylquinoline*, identical with the product of Beyer condensation on 2 : 5-dichloroaniline.

That the ortho-para directive influence of the chlorine atoms in these compounds operates is shown by the results of nitrating 6- and 7-chloro-2 : 4-dimethylquinoline. The effect of 5 : 8-reactivity in the quinoline series is shown very clearly by the fact that 6-bromoquinoline sulphonates in position 8 (Edinger, *Ber.*, 1908, **41**, 937), whilst 6-chloroquinoline sulphonates either in 5 or in 8, according to conditions (Claus and Schedler, *J. pr. Chem.*, 1894, **49**, 355). An even more striking case is that recorded by Kaufmann and Hussy (*Ber.*, 1908, **41**, 1735), who showed that 6- and 7-nitroquinoline nitrate to give, respectively, 5 : 6- and 6 : 8-, and 5 : 7- and 7 : 8-

* The chlorine atom here appears to be of the positive type.

dinitroquinoline, *i.e.*, 5 : 8-reactivity causes some nitration to occur in the ortho-position to a nitro-group.

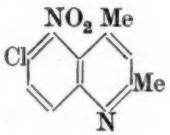
Dichloro-derivatives of 2 : 4-dimethylquinoline also nitrate quantitatively to give only one product. Thus the 5 : 8-dichloro-derivative gives 5 : 8-*dichloro*-6-*nitro*-2 : 4-*dimethylquinoline*, whose constitution is proved by its conversion, through the corresponding 6-*amino*-compound, into 5 : 6 : 8-*trichloro*-2 : 4-*dimethylquinoline*, also obtained by Beyer condensation of 2 : 4 : 5-trichloroaniline. Nitration of other dichloro-compounds undoubtedly occurs in position 5 or 8, but it has been impossible to prove the constitutions of the products, since the amines obtained by reduction could not be converted into the corresponding chloro-compounds. We have confirmed the observation made by Claus (compare *J. pr. Chem.*, 1894, **49**, 355) that the Sandmeyer reaction is unsuitable in the quinoline series, whereas the Gattermann method gives good results. On the other hand, the success of a replacement of an amino-group by chlorine depends also on the basicity of the amino-compound, and on the rate of diazotisation of the hydrochloride; for example, whilst 8-amino-, 6-*chloro*-5-*amino*-, 8-chloro-5-amino-, and 7-*chloro*-8-*amino*-2 : 4-*dimethylquinoline* diazotise readily, 5 : 8-dichloro-6-amino-2 : 4-dimethylquinoline diazotises slowly, 6 : 8-*dichloro*-5(?)-*amino*- still more slowly, and 5 : 6-*dichloro*-8(?)-*amino*- hardly at all. 5 : 6 : 8-Trichloro-2 : 4-dimethylquinoline does not undergo nitration under the conditions employed.

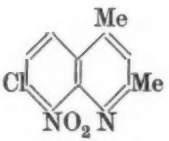
It was stated above that 3 : 4-dichloroaniline was converted by the Combes reaction into 6 : 7-dichloro-2 : 4-dimethylquinoline, but this fact was only established with considerable difficulty. *o*-Dichlorobenzene was found to condense readily with acetyl chloride under Friedel–Crafts conditions to give 3 : 4-*dichloroacetophenone*, but the nitration of the latter caused unexpected difficulties. These were finally overcome, and the 3 : 4-*dichloro*-2-*nitroacetophenone* obtained was converted into the corresponding *amino*-compound, which, when heated with acetone and a trace of alkali, gave an almost quantitative yield of 6 : 7-dichloro-2 : 4-dimethylquinoline, m. p. 119—120°, identical with the product from 3 : 4-dichloroaniline. The proof of the constitution of this product enabled us to deduce the constitution of the product of nitration of 6-chloro-2 : 4-dimethylquinoline. When this was reduced and the resulting amine was submitted to the Gattermann reaction, a dichlorodimethylquinoline was obtained, also melting at 119—120°; this depressed the m. p. of the synthetic 6 : 7-isomeride, and was therefore 5 : 6-dichloro-2 : 4-dimethylquinoline, since the 6 : 8-isomeride, obtained by Beyer condensation of 2 : 4-dichloroaniline, melted at 148—148·5°.

The chloro-2 : 4-dimethylquinoline obtained by the Combes reaction from *m*-chloroaniline, and therefore either the 5- or the 7-derivative, gave a nitro-compound which was converted into a chloroamino-compound, and thence into a dichloro-compound melting at 104—104·5°. The latter could only be 5 : 6-, 5 : 7-, 5 : 8-, 6 : 7-, or 7 : 8-dichloro-2 : 4-dimethylquinoline. Of these compounds, three were already known, and 5 : 7-*dichloro*-2 : 4-*dimethylquinoline*, obtained by Beyer condensation from 3 : 5-dichloroaniline, was found to melt at 84—86°. It therefore follows that the above chlorodimethylquinoline is the 7-derivative, and the derived dichlorodimethylquinoline the 7 : 8-derivative.

6-*Chloro*-5-*nitro*-2 : 4-*dimethylquinoline* was found not to react with piperidine, and this led us to consider again the work of Mills and Smith (*loc. cit.*). If, with these authors, we assume the presence of a central double bond in the quinoline molecule, the 6-chlorine atom and the 5-nitro-group will be attached to carbon atoms joined by a double bond (XVII), a condition assumed by Borsche and his co-workers (*Annalen*, 1913, **402**, 81; 1926, **447**, 1) to be associated with diminished reactivity of chlorine. One of these assumptions—we think that due to Borsche—appears to be incorrect, since 7-*chloro*-8-*nitro*-2 : 4-*dimethylquinoline* (XVIII), in which almost similar conditions obtain, reacts readily with piperidine to give 8-*nitro*-7-*piperidino*-2 : 4-*dimethylquinoline*.

(XVII.)





(XVIII.)

We have also investigated the chlorination of various chloro-derivatives of 2 : 4-dimethylquinoline in presence of glacial acetic acid and anhydrous sodium acetate. 7-Chloro-2 : 4-dimethylquinoline gave a *trichloro*-derivative, whilst 6- and 8-chloro- and 5 : 6-dichloro-2 : 4-dimethylquinoline gave *tetrachloro*-2 : 4-*dimethylquinolines*, all different. 5 : 8-Dichloro-2 : 4-dimethylquinoline, however, gave a *pentachloro*-2 : 4-*dimethylquinoline*, identical with the product of chlorinating the 6 : 8-compound. All these compounds contain mobile chlorine (of the negative type), showing that chlorination has occurred partly in the methyl groups. Similar compounds were obtained by Königs from 8-nitro-4-methylquinoline (*Ber.*, 1898, **31**, 2368) and later by Hammick (J., 1923, **123**, 2882). Little can be said with regard to the constitutions of our compounds, except that the pentachloro-compound must, because of its dual origin, contain chlorine atoms in the 5-, 6-, and 8-positions. The

extent to which chlorination occurs is apparently determined neither by the amount of sodium acetate used, nor by the solubility of the compounds actually isolated.

EXPERIMENTAL.

Condensation of Substituted Anilines with Acetylacetone.—The general method adopted was to allow a mixture of the substituted aniline (1 mol.) with 1·1 mols. of acetylacetone to boil gently under reflux for 1—2 hours. The cooled product was then thoroughly shaken with water, benzene added, and the two layers separated. The benzene solution was shaken twice or thrice with water, dried over anhydrous sodium sulphate, and heated at 100° until free from benzene. In most cases, the anil was then pure enough to solidify when cooled.

p-Toluidine.—The anil was obtained in almost theoretical yield, and after one crystallisation from light petroleum (b. p. 40—60°) formed massive prisms, m. p. 68—69°. Combes (*loc. cit.*) gave m. p. 39—40°, whereas in D.R.-PP. 363,582 and 363,583 the m. p. is given as 65·5°. Ferriss and Turner (J., 1920, **117**, 1140) stated that the anil was converted, under the conditions now given for its formation, into 2 : 4 : 6-trimethylquinoline. This, however, is not the case. The anil, β-*p*-toluidinopropenyl methyl ketone, when treated with sulphuric acid by the usual method (see below) was quantitatively converted into 2 : 4 : 6-trimethylquinoline, m. p. 43—45°. The m. p. (63—64°) quoted by Pfitzinger (*J. pr. Chem.*, 1888, **38**, 40) is evidently that of the hydrate, which we have found to melt at 63—65°. The concentrated sulphuric acid solution of the crude quinoline, when treated with potassium dichromate, remained a clear reddish-brown colour after some minutes' boiling, indicating the absence of even small quantities of *p*-toluidine. Such quantitative conversion into a quinoline was not observed with the product from any other substituted aniline.

o-*Chloroaniline.*—β-o-*Chloroanilinopropenyl methyl ketone* was readily formed, and separated from light petroleum (b. p. 40—60°) in small plates, m. p. 66—67° (Found: Cl, 17·1. $C_{11}H_{12}ONCl$ requires Cl, 16·9%).

p-*Chloroaniline.*—β-p-*Chloroanilinopropenyl methyl ketone* was readily obtained, and crystallised from light petroleum (b. p. 40—60°) in rectangular prisms, m. p. 60—61° (Found: Cl, 17·0%).

m-*Chloroaniline.*—β-m-*Chloroanilinopropenyl methyl ketone*, readily formed, crystallised from light petroleum (b. p. 40—60°) in plates; it had m. p. 42°, and b. p. 187°/13 mm. (Found: N, 6·9. $C_{11}H_{12}ONCl$ requires N, 6·7%).

o-*Hydroxybenzylidene*-3-*chloroaniline* was readily obtained, and separated from alcohol in bright yellow needles, m. p. 99° (Found : N, 6·1. $C_{13}H_{10}ONCl$ requires N, 6·0%).

2 : 4-*Dichloroaniline*.—This base condensed readily with acetylacetone. β-2 : 4-*Dichloroanilinopropenyl methyl ketone* separated from aqueous alcohol in needles, m. p. 100·5° (Found : N, 5·8. $C_{11}H_{11}ONCl_2$ requires N, 5·7%). o-*Hydroxybenzylidene*-2 : 4-*dichloroaniline* separated from alcohol in brilliant yellow needles, m. p. 90·5° (Found : N, 5·3. $C_{13}H_9ONCl_2$ requires N, 5·3%).

2 : 5-*Dichloroaniline*.—The condensation of this base with acetylacetone presents two interesting features. When any other of the substituted anilines dealt with was heated with acetylacetone at 100° (the approximate b. p. of such mixtures), water was seen to separate after a few minutes. In the case of 2 : 5-dichloroaniline, however, water only separated from the condensation mixture when the latter was boiling briskly. On cooling it a few degrees, the water redissolved. The second peculiarity observed was the small yield obtained, so that the β-2 : 5-*dichloroanilinopropenyl methyl ketone* was only isolable by distillation under diminished pressure (b. p. 190—200°/15 mm.) of the purified reaction product. It finally crystallised from light petroleum (b. p. 40—60°) in octahedra, m. p. 46°. *o*-Hydroxybenzylidene-2 : 5-dichloroaniline, on the other hand, was readily obtainable in good yield; the crude product crystallised from alcohol in bright yellow needles, m. p. 107° (Found : N, 5·4%).

3 : 5-*Dichloroaniline*.—Condensation occurred readily, but the β-3 : 5-*dichloroanilinopropenyl methyl ketone* was not obtained crystalline. The 3 : 5-dichloroaniline required was obtained by reducing 3 : 5-dichloronitrobenzene by the iron method, the nitro-compound being prepared as follows (compare Holleman and Reiding, *Rec. trav. chim.*, 1904, **23**, 366) : A mixture of 85 g. of 2 : 6-dichloro-4-nitroaniline and 170 c.c. of concentrated sulphuric acid was diazotised at −5° with 56 g. of solid sodium nitrite. The dark paste obtained was slowly run into 600 c.c. of boiling 96% alcohol; immediate decomposition then took place, with the formation of an orange solution. Some sodium sulphate separated, and on diluting the mixture largely with water, the nitro-compound was precipitated. It had m. p. 62—65°, whereas the pure substance melts at 65°.

3 : 4-*Dichloroaniline*.—This base condensed smoothly with acetylacetone to give β-3 : 4-*dichloroanilinopropenyl methyl ketone*, which separated from alcohol in almost colourless needles, m. p. 73° (Found : N, 5·7%). o-*Hydroxybenzylidene*-3 : 4-*dichloroaniline* crystallises from alcohol in long, yellow needles, m. p. 113°

(Found: N, 5·4%). The 3 : 4-dichloroaniline required was prepared by reducing the corresponding nitro-compound by the iron method.

o-*Anisidine.*—Condensation occurred readily to give β-o-*methoxyanilinopropenyl methyl ketone*, which separated from light petroleum (b. p. 40—60°) in plates, m. p. 51—52·5°.

3-*Chloro*-6-*acetamidoaniline.*—This also was found to condense with acetylacetone, but the product, like that from *o*-anisidine, was not further examined, since it gave no quinoline derivative when treated with concentrated sulphuric acid.

3 : 4-*Dichloro*-6-*nitroaniline.*—This base was recovered unchanged after being heated with excess of acetylacetone in a closed tube for 6 hours at 200°. The dichloro-base was readily obtainable by hydrolysing (90% sulphuric acid at 120° for 20 minutes) the corresponding acetyl derivative, the latter being prepared as described by Beilstein and Kurbatow (*Annalen*, 1879, **196**, 225).

Attempted Preparation of 2 : 3-*Dichloroaniline.*—(*a*) The nitration of 3 : 4-dichloroaniline in presence of a large excess of sulphuric acid led to a mixture of products, from which only unchanged base was isolated. It had been hoped that 3 : 4-dichloro-5-nitroaniline would be obtained, and thence, by removal of the amino-group, 2 : 3-dichloronitrobenzene. (*b*) *o*-Chloroacetanilide sulphonated readily when added to cold fuming sulphuric acid (25% SO_3). The solution was treated with nitric acid, and then evidently contained 3-chloro-5-nitro-4-acetamidobenzenesulphonic acid (compare D.R.-P. 206,345, dealing with a similar treatment of *m*-chloroacetanilide). The solution of the nitrosulphonic acid, when diluted slightly and boiled, contained acetic acid, but various methods tried did not give detectable quantities of 2-chloro-6-nitroaniline, from which it had been hoped to prepare 2 : 3-dichloronitrobenzene.

Conversion or Attempted Conversion of Anils of Acetylacetone into Substituted 2 : 4-*Dimethylquinolines.*—The most satisfactory method of effecting this condensation was as follows: The anil was slowly added, as a fine powder, or as a thin stream of liquid, to six times its weight of concentrated sulphuric acid, the latter being kept well shaken, and cooled below 5°. As soon as solution occurred, the mixture was heated for 0·5 hour on the boiling water-bath. The extent of condensation was readily diagnosed by diluting a little of the sulphuric acid solution. In cases of unsuccessful condensation, the odour of acetylacetone became apparent at once, and, usually, the sulphate of the unchanged base separated. Neither of these observations was made in the case of a successful condensation, and the further addition of potassium dichromate then gave an immediate precipitate of the quinoline dichromate

(see above under *p*-toluidine). The isolation of the quinolines presented no difficulty.

β-*Anilinopropenyl Methyl Ketone*.—The yield of pure 2 : 4-dimethylquinoline obtained was 90% on the weight of anil taken, or 75% on the weight of aniline. The success of this condensation appears to depend largely on the purity of the anil, the distillation of which (Combes, *loc. cit.*) is not only unnecessary, but disadvantageous.

The anils from acetylacetone and *o*- and *p*-chloroaniline, 2 : 4-, 2 : 5-, and 3 : 5-dichloroaniline, *o*-anisidine and 3-chloro-6-acetamidoaniline were not converted into the corresponding quinolines by the sulphuric acid method. Use of absolute sulphuric acid, or of slightly fuming acid, or variation of the temperature of heating made no difference to the result.

The anil from 2 : 5-dimethoxyaniline behaved exactly as described by Lions, Perkin, and Robinson (*loc. cit.*), the yield of 5 : 8-dimethoxy-2 : 4-dimethylquinoline being almost quantitative.

β-m-*Chloroanilinopropenyl Methyl Ketone*.—This anil (compare that last mentioned) was converted almost quantitatively into 7-*chloro*-2 : 4-*dimethylquinoline*, the *hydrate* of which separated from aqueous alcohol in colourless needles, m. p. 61° (Found : Cl, 16·7. $C_{11}H_{10}NCl$ requires Cl, 18·5%. $C_{11}H_{10}NCl,H_2O$ requires Cl, 16·9%). Crystallisation of the hydrate from light petroleum afforded the anhydrous base in prismatic needles, m. p. 46·5—48·5° (Found : Cl, 17·9%). The quinoline is obtained in almost theoretical yield if the anil–sulphuric acid solution is heated, not at 100°, but at 130—140°.

7-*Chloro*-2 : 4-*dimethylquinoline hydrochloride* forms colourless needles, m. p. 277° (decomp.), soluble in water [Found : Cl (ionisable), 15·8. $C_{11}H_{10}NCl,HCl$ requires Cl (ionisable), 15·6%]. The *sulphate* separates from water in rhombohedra, and the *dichromate* in brilliant yellow needles. The *silver nitrate additive compound*, colourless needles [Found : Ag, 17·8. $(C_{11}H_{10}NCl)_2,AgNO_3$ requires Ag, 17·6%] melts at 197° (decomp.).

In an attempt to synthesise this quinoline, various experiments were carried out on the preparation of 4-chloro-2-aminoacetophenone. (1) This substance could not be isolated from the product of interaction of *p*-chloroaniline with acetic anhydride in presence of zinc chloride, although aniline, under similar conditions, is known to afford *p*-aminoacetophenone (Klingel, *Ber.*, 1885, **18**, 2688). (2) 2 : 4-Dinitroethylbenzene was not converted into 2 : 4-dinitroacetophenoneoxime when kept at room temperature in presence of amyl nitrite and piperidine, although Reich and Nicolaeva (*Helv. Chim. Acta*, 1919, **2**, 84) obtained a small yield of the oxime by using

sodium ethoxide as the condensing agent. (3) 2 : 4-*Dichloroacetophenone* was not converted into 4-chloro-2-aminoacetophenone when heated for 6 hours at 180° with alcoholic ammonia. The 2 : 4-dichloroacetophenone was obtained in 15% yield by condensing *m*-dichlorobenzene with acetyl chloride in presence of aluminium chloride. The majority of the dichlorobenzene was recovered unchanged. 2 : 4-Dichloroacetophenone has m. p. 33—34°, and b. p. 140—150°/15 mm. (Found : Cl, 37·2. $C_8H_6OCl_2$ requires Cl, 37·5%). To a boiling suspension of 1 g. of the ketone in 100 c.c. of 1·5% aqueous sodium hydroxide, were added 2·23 g. of potassium permanganate dissolved in 50 c.c. of water. Immediate oxidation occurred, and the sole product obtained, after crystallisation from aqueous alcohol, was 2 : 4-dichlorobenzoic acid, m. p. 161—162°.

β-3 : 4-*Dichloroanilinopropenyl Methyl Ketone*.—The only successful condensation of this compound was carried out by slowly adding the anil to five times its weight of cooled concentrated sulphuric acid, and heating the resulting solution at 130—140° for 4 hours. On cooling and pouring the mixture into water, a little 3 : 4-dichloroaniline sulphate separated; this was collected. The filtrate was rendered alkaline with ammonia, the precipitated quinoline was removed and dissolved in dilute sulphuric acid, and dilute potassium dichromate solution added. The precipitated *dichromate* (yellow needles, soluble in hot, but insoluble in cold water) was collected, and converted into the free base, which, after crystallisation from alcohol or light petroleum (b. p. 80—100°), formed colourless needles, m. p. 119—120° (Found : Cl, 31·5. $C_{11}H_9NCl_2$ requires Cl, 31·4%). Repetition of this condensation some dozen times under apparently similar conditions never gave rise on any second occasion to isolable quantities of the quinoline. Variation of the concentration of sulphuric acid, or of temperature or of time of heating, or of the conditions of mixing of anil and acid, also led to the same negative result. Saturation of a glacial acetic acid solution of the anil with dry hydrogen chloride (compare Bülow and Issler, *loc. cit.*) or treatment of a similar solution with acetic anhydride, or with acetyl chloride, did not cause ring-closure. The anil was also heated with syrupy phosphoric acid at 130—145° and then at 200° for 2 hours, but after this treatment, only 3 : 4-dichloroaniline was isolated. In the case of the acetyl chloride experiment, a crystalline solid separated after 5 minutes, but then redissolved. Treatment of the anil with a mixture of acetic anhydride and acetyl chloride merely led to the production of 3 : 4-dichloroacetanilide.

6 : 7-*Dichloro*-2 : 4-*dimethylquinoline hydrochloride* forms white needles, m. p. 235°, sparingly soluble in water [Found : Cl (ionisable), 13·6. $C_{11}H_9NCl_2,HCl$ requires Cl (ionisable), 13·5%]. The

chloroaurate forms twig-like, yellow needles, sparingly soluble even in hot water; the *sulphate* forms white needles; the *silver nitrate additive compound* is precipitated when an alcoholic solution of the base is treated with an aqueous solution of silver nitrate. It forms colourless needles, m. p. 218—219°, soluble in hot, but sparingly soluble in cold, alcohol [Found: Ag, 17·7. $(C_{11}H_9NCl_2)_2,AgNO_3$ requires Ag, 17·4%].

Nitration of 6 : 7-*Dichloro*-2 : 4-*dimethylquinoline*.—The method used for nitrating this base, and for all the other quinoline bases mentioned, unless otherwise stated, was as follows: The base was added slowly to five times its weight of a mixture, kept at −5°, of 1 part by weight of fuming nitric acid (*d* 1·5) and 2 parts by weight of concentrated sulphuric acid (*d* 1·84). The resulting solution was kept at the ordinary temperature for 1—2 hours and then poured on ice, and the nitro-compound was isolated either as the sulphate or as the free base.

In the case of 6 : 7-*dichloro*-8(?)-*nitro*-2 : 4-*dimethylquinoline*, the base was crystallised from alcohol, and then formed white needles, m. p. 197° (Found: N, 10·6. $C_{11}H_8O_2N_2Cl_2$ requires N, 10·4%). Nitration of 6 : 7-dichloro-2 : 4-dimethylquinoline with mixed acid at 60° also gave the nitro-compound described above.

Consideration of the other results obtained in this work suggests that the nitro-compound is of the 8- rather than of the 5-type.

Preparation of Substituted 2 : 4-*Dimethylquinolines by the Beyer Process*.—The method adopted was essentially that used by Beyer (*loc. cit.*), but in detail as follows: (*a*) A mixture of 96 g. of paraldehyde and 160 g. of acetone was saturated with dry hydrogen chloride, and left for 3 days. Such a mixture then weighed approximately 425 g. (*b*) The substituted aniline (1 mol.) was thoroughly ground with 3 mols. of concentrated hydrochloric acid, and the mixture added to one of 0·5 mol. of nitrobenzene and 255 g. of the acetone–paraldehyde–hydrogen chloride mixture. The whole was heated at 100° under reflux for 10 hours, and then worked up by an appropriate method, as described under individual compounds.

8-*Chloro*-2 : 4-*dimethylquinoline*.—The reaction mixture obtained from *o*-chloroaniline by the process just mentioned was poured into water; the resulting mixture was repeatedly extracted with ether, and the aqueous-acid layer rendered alkaline with sodium hydroxide. It was then thoroughly extracted with ether, and the ethereal extract was washed with brine and dried over anhydrous sodium sulphate. Evaporation of the ether and distillation of the residue under diminished pressure afforded two fractions, the first consisting of 40% of the original chloroaniline used; the second, b. p. 170—190°/15 mm. (mainly 185°/15 mm.), was 8-*chloro*-

2 : 4-*dimethylquinoline* (yield 25%), which solidified on cooling. After being twice crystallised from light petroleum (b. p. 40—60°), it formed stout, white prisms, m. p. 74° (Found : Cl, 18·6. $C_{11}H_{10}NCl$ requires Cl, 18·6%). The quinoline separates anhydrous from aqueous alcohol in small, rectangular plates. It was unaffected by piperidine after 1 hour's heating at 100°.

Nitration of 8-*Chloro*-2 : 4-*dimethylquinoline*.—The last-named quinoline nitrated readily, and on pouring the nitration mixture on ice a copious white precipitate of the *sulphate* of 8-chloro-5-nitro-2 : 4-dimethylquinoline was obtained. This was collected and treated with aqueous ammonia, and the reddish-brown solid obtained was crystallised from alcohol. The nitro-compound forms pale yellowish-brown prisms, m. p. 107—108° (Found : Cl, 15·1. $C_{11}H_9O_2N_2Cl$ requires Cl, 15·0%) (yield, more than 90%).

8-*Chloro*-5-*amino*-2 : 4-*dimethylquinoline* was prepared by the reduction of the 5-nitro-compound with iron, water, and ferric chloride. The reaction mixture was cooled and filtered. The residue of iron and amino-compound was dried and extracted with benzene. The *amino-compound* separated from the cooled benzene solution in brown prisms, m. p. 170—172° (Found : Cl, 17·1. $C_{11}H_{11}N_2Cl$ requires Cl, 17·2%) (yield, 33%).

Conversion of 8-*Chloro*-5-*amino- into* 5 : 8-*Dichloro*-2 : 4-*dimethylquinoline*.—The chloroamino-compound (4 g.) was ground with 12 c.c. of concentrated hydrochloric acid, and the stiff reddish-brown paste so obtained cooled to −5°. A solution of 1·4 g. of sodium nitrite in 4·5 c.c. of water was slowly added. Diazotisation was rapid, and to the clear solution obtained was added a suspension of 5 g. of copper powder in hydrochloric acid (1 vol. of concentrated acid : 1 vol. of water). A brisk evolution of nitrogen occurred. Removal of the copper left a yellowish solution, which when treated with aqueous ammonia gave an almost theoretical yield of 5 : 8-dichloro-2 : 4-dimethylquinoline as a white precipitate. This, after being twice crystallised from alcohol, formed prismatic needles, m. p. 117—118°, alone or when mixed with 5 : 8-dichloro-2 : 4-dimethylquinoline prepared from 2 : 5-dichloroaniline (see below).

Chlorination of 8-*Chloro*-2 : 4-*dimethylquinoline*.—A solution of 1 g. of the quinoline in 20 c.c. of glacial acetic acid was heated at 60°, saturated with chlorine, and then treated with water. The white precipitate of the *tetrachloro*-compound obtained, after being twice crystallised from alcohol, formed slender needles, m. p. 150—152° (Found : Cl, 47·5. $C_{11}H_7NCl_4$ requires Cl, 48·1%).

6-*Chloro*-2 : 4-*dimethylquinoline*.—The Beyer reaction mixture from *p*-chloroaniline was poured into water, and the product was extracted with ether. The aqueous layer was evaporated to about one-third

of its original volume; a crystalline precipitate of crude hydrochloride was slowly deposited. This was collected, extracted with boiling acetone to remove colouring matter, and then treated with warm aqueous ammonia. The almost pure base so obtained separated from light petroleum (b. p. 80—100°) in stout prisms, m. p. 98—99° (Found: Cl, 16·4%) (yield, 16%). The quinoline crystallises from aqueous alcohol as the *hydrate*, silky needles, m. p. 84—85·5° (Found: Cl, 17·0. $C_{11}H_{10}NCl,H_2O$ requires Cl, 16·9%). The mother-liquor from which the above crude hydrochloride separated was found to contain only *p*-chloroaniline hydrochloride.

The quinoline forms an orange-yellow *dichromate*, which may be crystallised from water.

Nitration of 6-*Chloro*-2 : 4-*dimethylquinoline*.—The nitration mixture, when poured on ice, afforded a crystalline precipitate of the *sulphate* of 6-*chloro*-5-*nitro*-2 : 4-*dimethylquinoline*, which was filtered off and decomposed with warm aqueous ammonia. The practically pure base was then crystallised from alcohol, and formed canary-yellow prisms, m. p. 132—133° (Found: Cl, 15·8%) (yield over 90%). The chloronitro-compound was unaffected when heated for 10 minutes at 100° with excess of piperidine.

6-*Chloro*-5-*amino*-2 : 4-*dimethylquinoline*.—The preceding nitro-compound was reduced with iron powder, aqueous alcohol, and ferric chloride. The reaction mixture was filtered while still hot, the residual iron well washed with alcohol, and the alcoholic extracts and filtrate were evaporated. The solid that separated on cooling crystallised from benzene in pale yellow, prismatic needles, m. p. 131—133° (Found: Cl, 17·2%) (yield, 52%).

Conversion of 6-*Chloro*-5-*amino- into* 5 : 6-*Dichloro*-2 : 4-*dimethylquinoline*.—The base (9·1 g.) was ground with 30 c.c of concentrated hydrochloric acid, and the resulting canary-yellow hydrochloride paste was treated at −5° with a solution of 3·1 g. of sodium nitrite in 5 c.c. of water. Diazotisation was rapid, and to the clear solution so obtained copper and hydrochloric acid were added as usual. The whole assumed a dirty green colour, and suddenly set to a stiff paste. Two volumes of water were then added, the whole was heated to boiling and filtered, and the filtrate was cooled. The resulting yellowish-brown hydrochloride (prisms) was collected and digested with aqueous ammonia. The base so obtained (6 g.), after being crystallised first from alcohol and then from light petroleum (b. p. 80—100°), formed stout, colourless prisms, m. p. 119—120° (Found: Cl, 30·9. $C_{11}H_9NCl_2$ requires Cl, 31·4%). A mixture of this quinoline (then of unknown constitution) with the 6 : 7-dichloro-isomeride (also then of unknown constitution) melted at about 90°.

Chlorination of 6-*Chloro*-2 : 4-*dimethylquinoline*.—A solution, heated at 60°, of 1 g. (1 mol.) of the chloro-compound in 20 c.c. of glacial acetic acid containing 2·2 g. (5 mols.) of fused sodium acetate was saturated with chlorine. No precipitate was formed, but on dilution an oily *tetrachloro*-compound was thrown down. This became solid on standing, and after being crystallised from aqueous alcohol, and then from light petroleum (b. p. 40—60°), formed slender needles, m. p. 75·5—81° (Found: Cl, 48·4. $C_{11}H_7NCl_4$ requires Cl, 48·1%).

Nitration of 5 : 6-*Dichloro*-2 : 4-*dimethylquinoline*.—When the nitration mixture was poured on ice, the free base was precipitated. It crystallised from alcohol, in which it was very sparingly soluble, in silky needles, m. p. 151—152·5° (Found: Cl, 26·2. $C_{11}H_8O_2N_2Cl_2$ requires Cl, 26·2%) (yield, over 90%).

5 : 6-*Dichloro*-8(?)-*amino*-2 : 4-*dimethylquinoline*.—The preceding nitro-compound readily underwent reduction when heated with iron powder, aqueous alcohol, and a little hydrochloric acid. The mixture was finally filtered, the residue well washed with alcohol, and the alcoholic filtrates diluted with water. The precipitated amino-compound (yield, 83%) was dried, and then melted at 118—120° (Found: Cl, 27·6. $C_{11}H_{10}Cl_2N_2$ requires Cl, 29·5%). The crude base was used for the succeeding experiment.

Attempted Conversion of 5 : 6-*Dichloro*-8(?)-*amino*-2 : 4-*dimethylquinoline into* 5 : 6 : 8(?)-*Trichloro*-2 : 4-*dimethylquinoline*.—A suspension of the amino-compound in concentrated hydrochloric acid did not appear to undergo diazotisation when treated with sodium nitrite. Subsequent addition of copper caused no evolution of nitrogen.

Chlorination of 5 : 6-*Dichloro*-2 : 4-*dimethylquinoline*.—When chlorine was passed into a solution of 1·1 g. of the quinoline (1 mol.) in 30 c.c. of glacial acetic acid containing 1·23 g. (3 mols.) of fused sodium acetate, a precipitate of a *tetrachloro*-compound was formed. This separated from alcohol, in which it was very sparingly soluble, in slender needles, m. p. 157—158° (Found: Cl, 48·3. $C_{11}H_7NCl_4$ requires Cl, 48·1%). A mixture of the tetrachloro-compound with the tetrachloro-compound (m. p. 150—152°) obtained from 8-chloro-2 : 4-dimethylquinoline melted below 130°.

Preparation of 7-*Chloro*-2 : 4-*dimethylquinoline by the Beyer Method*.—The reaction mixture obtained from *m*-chloroaniline was poured into water, and the resulting mixture extracted several times with ether. The aqueous layer was basified, and extracted with ether, and the ethereal extract was washed with brine and dried. Distillation of the contained basic mixture under diminished pressure afforded 55% of unchanged *m*-chloroaniline as a first

fraction, and then a 36% yield of crude chloroquinoline, b. p. about 174°/10 mm. The latter partly crystallised on prolonged standing, and the crystalline portion, isolated on porous porcelain, separated from light petroleum (b. p. 40—60°) in prismatic needles, m. p. 42—45°, either alone or when mixed with the product from *m*-chloroaniline and acetylacetone (above). A little of the 5-isomeride was presumably present in the crude basic mixture, but in insufficient quantity for isolation.

7-Chloro-2 : 4-dimethylquinoline was unaffected by piperidine after 1 hour's heating at 100°.

Nitration of 7-Chloro-2 : 4-dimethylquinoline.—For this purpose, the chloro-compound obtained by the more convenient acetylacetone method was used. Nitration, followed by pouring on ice, gave a precipitate of the almost pure *7-chloro-8-nitro-2 : 4-dimethylquinoline* (yield over 95%). Nitration with warm mixed acid gave a similar result, either product separating from alcohol in slender, white needles, m. p. 189—189·5° (Found : N, 12·0. $C_{11}H_9O_2N_2Cl$ requires N, 11·8%).

When the nitro-compound was heated for 0·5 hour at 100° with an excess of piperidine, piperidine hydrochloride separated, and on extensive dilution with water a yellow powder was obtained. This separated from alcohol, in which it was sparingly soluble even when hot, in prisms; a second crystallisation from light petroleum (b. p. 80—100°)–benzene afforded *8-nitro-7-piperidino-2 : 4-dimethylquinoline* in rectangular plates, m. p. 168—170°. When mixed with the original chloronitro-compound, the substance melted at about 140°.

7-Chloro-8-amino-2 : 4-dimethylquinoline.—This substance, which was practically insoluble in hot aqueous alcohol, rapidly dissolved at 90—100° in that solvent in presence of iron powder and a little ferric chloride. Filtration, extraction of the iron powder with alcohol, and evaporation gave a black oil which solidified on cooling, and then crystallised from light petroleum (b. p. 40—60°) in slender, pale yellow needles, m. p. 51—53° (yield 83%) (Found : Cl, 17·4%).

Conversion of 7-Chloro-8-amino-2 : 4-dimethylquinoline into 7 : 8-Dichloro-2 : 4-dimethylquinoline.—The amino-compound was ground with concentrated hydrochloric acid, and the bright yellow hydrochloride paste diazotised at −10° with aqueous sodium nitrite. The clear red diazo-solution tended to undergo spontaneous decomposition, producing a coppery-brown, amorphous solid, but when it was added to a solution of cuprous chloride in hydrochloric acid normal decomposition appeared to occur. The product was treated with excess of ammonia, and the precipitated solid was collected, dried, and extracted with light petroleum (b. p. 40—60°). 7 : 8-

Dichloro-2 : 4-*dimethylquinoline* was then obtained in slender, prismatic needles, m. p. 104—104·5° (yield under 20%) (Found: Cl, 30·7%).

Chlorination of 7-*Chloro*-2 : 4-*dimethylquinoline*.—Chlorination of this base by the usual method in the cold afforded a *trichloro*-2 : 4-*dimethylquinoline*, which separated from alcohol in colourless needles, m. p. 195° (Found: Cl, 41·0. $C_{11}H_8NCl_3$ requires Cl, 40·9%).

6 : 8-*Dichloro*-2 : 4-*dimethylquinoline*.—The condensation mixture obtained by applying the Beyer reaction to 2 : 4-dichloroaniline was poured into water, and the resulting mixture repeatedly extracted with ether. The aqueous layer was boiled until free from ether, and then basified. The solid precipitated, after being collected and dried, was extracted with hot light petroleum (b. p. 80—100°), from which solvent 6 : 8-dichloro-2 : 4-dimethylquinoline separated in slender needles, m. p. 148—148·5° (yield 20%) (Found: Cl, 31·4%). The base separated anhydrous from aqueous alcohol.

Nitration of 6 : 8-*Dichloro*-2 : 4-*dimethylquinoline*.—The nitration solution when poured into a large bulk of water gave a precipitate of crude 6 : 8-*dichloro*-5(?)-*nitro*-2 : 4-*dimethylquinoline*, which separated from alcohol in pale yellow prisms, m. p. 120—122°. A further crystallisation from light petroleum (b. p. 40—100°) raised the m. p. to 122—123° (yield, 80%) (Found: Cl, 26·7%).

6 : 8-*Dichloro*-5(?)-*amino*-2 : 4-*dimethylquinoline*.—Reduction of the corresponding nitro-compound was effected by the usual method, using aqueous alcohol. The iron residue was extracted with hot acetone, and the extracts were evaporated. Crystallisation of the residue from alcohol afforded white, rectangular plates, m. p. 194—195° (yield, 81%) (Found: Cl, 29·6%). The amino-compound was converted by concentrated hydrochloric acid into a stiff, orange hydrochloride paste, which diazotised very slowly. Addition of copper powder caused some nitrogen evolution, but only unchanged base was isolated when the product was worked up.

Chlorination of 6 : 8-*Dichloro*-2 : 4-*dimethylquinoline*.—A solution of 1 g. of the quinoline (1 mol.) in 20 c.c. of glacial acetic acid containing 0·36 g. (1 mol.) of fused sodium acetate was heated at 60°, and saturated with chlorine. The precipitated solid separated from alcohol in needles, m. p. 124—125°, and was a *pentachloro*-quinoline. A mixture with the product obtained by the chlorination of 5 : 8-dichloro-2 : 4-dimethylquinoline (m. p. 127—128°) melted at 125—127°.

5 : 8-*Dichloro*-2 : 4-*dimethylquinoline*.—The product of the Beyer condensation using 2 : 5-dichloroaniline was poured into a large bulk of water, and the black, oily layer separated. The aqueous

layer was treated in the usual manner, and finally gave the dichloroquinoline as a solid, which separated from alcohol or from light petroleum (b. p. 80—100°) in prismatic needles, m.p. 117—118·5° (yield, 29%) (Found : Cl, 31·5%).

5 : 8-*Dichloro*-6-*nitro*-2 : 4-*dimethylquinoline*.—Nitration of the preceding quinoline, followed by dilution, afforded a precipitate which, after treatment with ammonia, separated from alcohol, in which it was very sparingly soluble, in white, slender needles, m. p. 155—157°. It separated from benzene in prisms (yield, over 90%) (Found : Cl, 26·3%).

5 : 8-*Dichloro*-6-*amino*-2 : 4-*dimethylquinoline*.—The nitro-compound underwent reduction with the usual reagents, in presence of aqueous alcohol. The iron residue was extracted for several hours with boiling benzene, the latter then evaporated, and the residue crystallised from benzene; the amino-compound was then obtained in brown octahedra, m. p. 192—193° (yield, 40%) (Found : Cl, 29·5%).

Conversion of 5 : 8-*Dichloro*-6-*amino- into* 5 : 6 : 8-*Trichloro*-2 : 4-*dimethylquinoline*.—The base was converted by concentrated hydrochloric acid into a paste consisting of yellow leaflets, which underwent diazotisation with difficulty. Addition of copper caused nitrogen evolution. Dilute hydrochloric acid was added, and then benzene, the latter to remove a black, tarry by-product. The acid solution, after being basified, gave a small quantity of a dark solid, which was boiled in alcoholic solution with charcoal, and after this treatment separated from alcohol, and later from light petroleum (b. p. 80—100°), in needles, m. p. 111—112·5°. A mixture of this compound with 5 : 6 : 8-trichloro-2 : 4-dimethylquinoline (see below) melted at 112—113·5°.

Chlorination of 5 : 8-*Dichloro*-2 : 4-*dimethylquinoline*.—Chlorination of this base at 60° in glacial acetic acid in presence of sodium acetate (1 mol.) afforded a pentachloroquinoline derivative as a precipitate, which separated, after two crystallisations from alcohol, in slender needles, m. p. 127—128° (Found : Cl, 54·0. $C_{11}H_6NCl_5$ requires Cl, 53·9%).

Preparation of 6 : 7-*Dichloro*-2 : 4-*dimethylquinoline by Beyer's Process*.—The reaction product obtained from 3 : 4-dichloroaniline when worked up in the usual manner gave about 55% of unchanged dichloroaniline, and a fraction, b. p. 180—190°/15 mm., which was evidently a mixture of 5 : 6- and 6 : 7-dichloro-2 : 4-dimethylquinoline. Separation by crystallisation of the dichromates gave a product, m. p. 80—105°, which was converted into a mixture of hydrochlorides. The latter was crystallised from dilute hydrochloric acid, and the hydrochloride of the 6 : 7-base so obtained was

treated with alkali. Crystallisation of the product from light petroleum (b. p. 80—100°) afforded a substance, m. p. 119—120°, which did not depress the m. p. of the quinoline obtained from acetylacetone (Found: Cl, 31·5%).

5 : 7-*Dichloro*-2 : 4-*dimethylquinoline*.—The reaction mixture from the Beyer condensation, using 3 : 5-dichloroaniline, was treated in the usual manner. Basification of the final acid solution gave a solid which was purified only with difficulty, but after being crystallised from light petroleum (b. p. 80—100°) and then from light petroleum (b. p. 60—80°) formed small prisms, m. p. 84—86° (yield, 20%) (Found: Cl, 31·5%).

On the first occasion of attempting this preparation, the paraldehyde–acetone–hydrogen chloride mixture used had been prepared 2 months previously. Condensation, followed by pouring into a large bulk of water, gave a black oil containing suspended solid. This was filtered and pressed, and then thoroughly extracted with a mixture of equal volumes of benzene and light petroleum (b. p. 80—100°). After decantation of the cooled extract, a yellowish-brown solid separated (31 g. from 50 g. of the dichloroaniline). It crystallised from alcohol in yellow leaflets, m. p. 168—169° (Found: Cl, 41·9, 42·0%). This *substance*, which will be examined later, was converted by aqueous ammonia into a second *substance*, which separated from light petroleum (b. p. 40—100°) in bunches of colourless needles, m. p. 69—70° (Found: Cl, 36·5, 36·6%). The second substance readily dissolved in hot dilute mineral acids, the solutions depositing crystalline precipitates on cooling.

5 : 6 : 8-*Trichloro*-2 : 4-*dimethylquinoline*.—Beyer condensation with 2 : 4 : 5-trichloroaniline gave a product, which, on pouring into water, afforded tarry material containing a solid in suspension. The aqueous portion, when basified, deposited tarry material only. The above solid was extracted with boiling hydrochloric acid (concentrated acid : water, 1 : 1), and tar removed. On cooling, 2 : 4 : 5-trichloroaniline hydrochloride separated, and this was removed. The mother-liquor, on basification, afforded the crude trichloroquinoline, which then separated from alcohol and later from light petroleum (b. p. 80—100°) in small, prismatic needles, m. p. 113—114° (Found: Cl, 41·5. $C_{11}H_8NCl_3$ requires Cl, 40·9%). The quinoline does not form a hydrate, and when dissolved in the usual manner in a mixture of nitric and sulphuric acids remained unchanged.

Beyer Condensation with o-*Nitroaniline*.—The condensation product was treated in the usual manner. At the basification stage, a brown, tarry solid was obtained. This readily dissolved in hot alcohol to give a solution, which on cooling deposited crystals.

These dissolved only with difficulty in fresh hot alcohol, from which solvent a *substance* separated in prismatic needles, m. p. 145—147° (12 g. from 35 g. of *o*-nitroaniline).

Beyer Condensation with p-*Nitroaniline.*—The condensation product, when poured into water, deposited a black tar, which was rejected. The aqueous layer was repeatedly extracted with benzene, the latter removed, and alkali added. The *substance* so obtained then separated from alcohol in brownish leaflets, m. p. 159—162° (31 g. from 50 g. of *p*-nitroaniline). This compound and that obtained from *o*-nitroaniline are under investigation.

When *m*-nitroaniline was submitted to the Beyer condensation, only unchanged base was isolated. 3-Chloro-6-nitroaniline and 3 : 4-dichloro-6-nitroaniline, on the other hand, were converted into unworkable tarry products.

3 : 4-*Dichloroacetophenone.*—A mixture of 251 g. of *o*-dichlorobenzene and 229 g. of anhydrous aluminium chloride was slowly treated with 133 g. of acetyl chloride and then heated at 100° for 3 hours. The product was poured on ice, hydrochloric acid added, and the oily material extracted with carbon tetrachloride. Vacuum distillation afforded 130 g. of pure 3 : 4-*dichloroacetophenone*, b. p. 135°/12 mm. (yield, 40%). This became solid on cooling, and then separated from light petroleum (b. p. 80—100°) in bunches of white needles, m. p. 76° (Found : Cl, 37·6. $C_8H_6OCl_2$ requires Cl, 37·5%).

When 2 : 4 : 5-trichlorobenzene was treated in a similar manner, it was unaffected.

Nitration of 3 : 4-*Dichloroacetophenone.*—When the ketone was dissolved either in nitric acid (*d* 1·5) kept at 10—15°, or in a mixture of glacial acetic and fuming nitric acids, it was unaffected. When it was heated with the fuming acid at 50—55°, it was extensively oxidised. Addition of fuming nitric acid to a solution of the ketone in acetic anhydride at 60—70° effected no change. A mixture of fuming nitric and concentrated sulphuric acids at −10° did not affect the ketone, but at 15° caused resinification. A large number of variations of these experiments gave similar results. Finally, nitration was effected by the following method : The ketone was added in small portions to seven times its weight of nitric acid (*d* 1·5), the temperature being allowed to rise to 35—38°, but not above 40°. The solution was kept for 5 minutes, the temperature being maintained between 35° and 38°, and was then poured into a large bulk of water. 3 : 4-*Dichloro-2-nitroacetophenone* separated as a pale yellow solid, which was collected, washed, and crystallised from alcohol. It formed irregular plates, m. p. 100—102° (Found : Cl, 30·4. $C_8H_5O_3NCl_2$ requires Cl, 30·4%).

3 : 4-*Dichloro*-2-*aminoacetophenone*.—The nitro-compound underwent rapid and almost quantitative reduction when heated with iron powder, water, and a little ferric chloride. The cooled mixture was filtered, and the solid residue repeatedly extracted with benzene. After concentration of the extract, the amino-compound separated on cooling in yellow prisms, the m. p., 154—156°, of which was not affected by a further crystallisation from acetone (Found: Cl, 34·8. $C_8H_7ONCl_2$ requires Cl, 34·9%).

Condensation of 3 : 4-*Dichloro*-2-*aminoacetophenone with Acetone*.—(*a*) When the amino-compound was heated under reflux in acetone solution, together with a little piperidine, for 6 hours, it was unaffected. (*b*) A mixture of the amino-compound (1 g.), acetone (3 c.c.), and 50% aqueous sodium hydroxide (0·2 c.c.) was heated in a closed tube for 6 hours at 185°. When cold, the tube contained a mass of brown crystals. The contents of the tube were extracted with boiling acetone, the extract was filtered, and the acetone evaporated. The solid residue then crystallised from light petroleum (b. p. 80—100°) in slightly brown needles, m. p. 119—120°. The substance produced no depression of the m. p. of the products obtained by the acetylacetone and Beyer methods (from 3 : 4-dichloroaniline) and was 6 : 7-dichloro-2 : 4-dimethylquinoline. A mixture with 5 : 6-dichloro-2 : 4-dimethylquinoline melted below 90°.

Nitration of 2 : 4-*Dimethylquinoline*.—A solution of the quinoline (102 g.) in 510 g. of concentrated sulphuric acid was slowly treated at 5° with 290 g. of the usual mixture of nitric and sulphuric acids (*i.e.*, an excess for mononitration. Addition of the last half of the mixed acid caused no temperature rise). The solution was poured on ice, and the resulting clear solution basified with ammonia. The precipitated 8-*nitro*-2 : 4-*dimethylquinoline* crystallised from alcohol in brown needles, m. p. 118—119° (yield 93%) (Found: N, 13·7. $C_{11}H_{10}O_2N_2$ requires N, 13·8%).

8-*Amino*-2 : 4-*dimethylquinoline*.—Reduction of the preceding nitro-compound by means of iron powder, water, and ferric chloride proceeded vigorously, but the product was difficult to purify. Repeated extraction with light petroleum (b. p. 80—100°) gave a solution from which tarry matter separated on cooling. When no more tar separated, light petroleum (b. p. 40—60°) was added, whereupon the amino-compound separated in brownish-yellow plates, m. p. 89—92° (yield, 26 g.) (Found: N, 15·9. $C_{11}H_{12}N_2$ requires N, 16·3%). The *picrate* separates from alcohol in bunches of yellow prisms. The sulphate is bright yellow, and sparingly soluble in water. A dilute sulphuric acid suspension diazotised readily, but on heating, the resulting solution gave a product other than the expected hydroxy-compound.

Conversion of 8-Amino- into 8-Chloro-2 : 4-dimethylquinoline.—(*a*) The base was diazotised in hydrochloric acid suspension. Addition of cuprous chloride–hydrochloric acid solution gave an indefinite product. (*b*) The amino-compound (17 g.) was ground with 50 c.c. of concentrated hydrochloric acid, and the resulting orange-red paste treated slowly at −5° with a solution of 6·6 g. of sodium nitrite in 10 c.c. of water. Diazotisation proceeded rapidly, with the formation of a clear solution, to which a suspension of copper powder in hydrochloric acid was added. Nitrogen was at once evolved, and the mixture was diluted with water and filtered. Addition of excess of ammonia gave a gummy precipitate, which was dissolved in a hot mixture of 25 c.c. of concentrated sulphuric acid and 125 c.c. of water. On cooling, the sulphate of 8-chloro-2 : 4-dimethylquinoline separated in pale yellow needles, which were collected, and decomposed with ammonia. The base so obtained, after crystallisation from aqueous alcohol and then from light petroleum (b. p. 40—60°), melted at 74°. A mixture with the base obtained by the Beyer method using *o*-chloroaniline melted at the same temperature.

Condensation of Dibenzoylmethane with Aniline.—A mixture of dibenzoylmethane (1 mol.) and *freshly distilled* aniline (1·25 mols.) was boiled under reflux for 9 hours. On cooling, the whole became solid, and was fractionally crystallised from alcohol. Colourless plates, m. p. 161°, separated first, and these did not depress the m. p. of benzanilide (Found : N, 7·6. Calc. : N, 7·1%). The mother-liquor finally yielded a solid, which separated from benzene–light petroleum in bright yellow prisms, m. p. 102—103° (Found : N, 4·1; *M*, cryoscopic in benzene, 288. Calc. : N, 4·7%; *M*, 299). This substance is evidently identical with that described by Watson (*loc. cit.*).

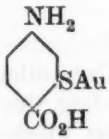
A few of the experiments described above were carried out by Mr. R. J. W. Smith, M.Sc. The authors desire to acknowledge the receipt of grants from the Research Fund of the Chemical Society in aid of the investigation.

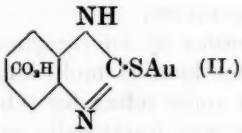
East London College,
University of London. [*Received, May 11th*, 1927.]

CCXL.—*Gold and Mercury Derivatives of 2-Thiolglyoxalines. Mechanism of the Oxidation of 2-Thiolglyoxalines to Glyoxalines.*

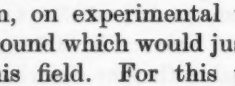
By Isidore Elkanah Balaban and Harold King.

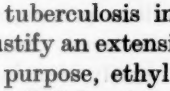
The application of compounds of gold to the treatment of tuberculosis starts from an old observation by Koch that inhibition of the growth of tubercle bacilli by gold cyanogen compounds occurs at a dilution of 1 in 2 million, but the question as to the chemotherapeutic efficacy of organic gold compounds in tuberculosis is still an open one. Two organic compounds of gold have attained considerable prominence in Germany for the treatment of tuberculosis, namely, 4-amino-2-aurothiolbenzoic acid (krysolgan) (I) (D.R.-P. 349012) and 2-aurothiolbenziminazolecarboxylic acid (triphal) (II) (E.P. 225875 of 1923), but there is no record of the cure of experimental infections of tuberculosis in animals by these substances.

(I.) 

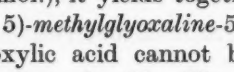
(II.) 

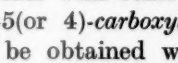
Both substances belong to a common type, of which an indefinite number could be prepared by synthesis, and the present communication is an attempt to determine whether there is any curative action, on experimental tuberculosis in animals, in this type of compound which would justify an extensive programme of syntheses in this field. For this purpose, ethyl 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylate (III) has been chosen as a starting point, as it is fairly readily accessible from ethyl acetoacetate.

(III.) 

(IV.) 

When treated in methyl-alcoholic solution with auric chloride (1/3 mol.), it yields together with other products *ethyl 2-aurothiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylate* (IV), from which the carboxylic acid cannot be obtained without decomposition and separation of gold. The ester (III) can, however, be hydrolysed to *2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylic acid* (V), which under similar conditions yields *2-aurothiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylic acid* (VI).

(V.) 

(VI.) 

The action of auric chloride on mercaptans was first studied by Zeise (*Ann. Physik*, 1834, **31**, 369), who, from the analysis of the amorphous product, C_2H_5SAu, of the action of auric chloride on ethyl mercaptan, considered that two atoms of chlorine were set free which acted on another portion of the mercaptan. In agreement with this, Hermann (*Ber.*, 1905, **38**, 2813), who examined the action of auric chloride on benzyl and *iso*amyl mercaptans, found the optimum conditions to be given by the equation

$$AuCl_3 + 3R{\cdot}SH = R{\cdot}SAu + RS{\cdot}SR + 3HCl.$$

The auromercaptides were amorphous and the disulphides were definitely identified.

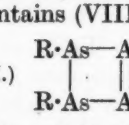
In the present instance, although the optimum conditions are determined by three molecular proportions of the thiolglyoxaline to one of auric chloride, the disulphide which should be produced in this reaction was never found, but only unchanged thiol acid. There is no doubt that the disulphide is initially produced, but, owing to the ease with which it acts as an acceptor for hydrogen, it is reduced during the subsequent operations necessary for its isolation. Attempts to make use of this ease of reversion of the disulphide to the thiol state, by using thiol acid and auric chloride in equimolecular proportion, to simplify the preparation of the 2-aurothiol acid (VI) which can be separated from the 2-thiol acid (V) only by a repetitive salting-out of the amorphous sodium salt of the aurothiol acid, were quite unsuccessful.

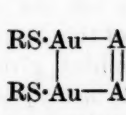
When auric chloride in methyl alcohol is added to the above-named thiolglyoxalines in methyl alcohol, there is invariably produced an intense blood-red coloration which persists for about 30 minutes and then fades to a pale yellow. There is no separation of gold. The same reaction is observed in aqueous hydrochloric acid solutions. It was first noted without comment by Gabriel and Pinkus (*Ber.*, 1893, **26**, 2203) for 2-thiol-4(or 5)-methylglyoxaline and by Tanret (*Compt. rend.*, 1909, **149**, 222) for ergothioneine, shown by Barger and Ewins (J., 1911, **99**, 2336) to be identical with 2-thiolhistidinebetaine. It is not, however, given by cysteine, thiocarbamide, allylthiocarbamide, or *p*-thiolphenylethylamine. We are not able to adduce any conclusive evidence as to the nature of this blood-red coloration. Whilst all the 2-thiolglyoxalines examined give the reaction instantaneously, 4(or 5)-*carbethoxy*-5(or 4)-*methylglyoxaline*-2-*disulphide* in methyl-alcoholic solution does not give it at once, but the colour gradually develops, lasts for many hours, and finally disappears. In hydrochloric acid solution the disulphide remains yellow for a few seconds on addition of chloroauric acid and then gives an amorphous, red precipitate

which becomes pale yellow after a few hours. One possibility is that the colour is due to the chromophoric influence of the sulphur atom on intermediate addition compounds of auric chloride with the thiolglyoxalines which gradually disappear as the auric chloride is used up in its reactions with the thiol group. This is supported by the observations of Wohl and Marckwald (*Ber.*, 1889, **22**, 1355), who found that platinum and gold chlorides formed with 2-thiol-1-methylglyoxaline brick-red and deep purple-red crystalline addition compounds, respectively, of the types, 2 base + $PtCl_4$, and base + $AuCl_3$, and of the present authors that the salt of 2-*ethylthiol*-4(or 5)-*methylglyoxaline* with chloroauric acid is red, whereas the addition compound of 2-phenyl-1-methylglyoxaline and auric chloride of the type base + $AuCl_3$ is deep yellow (J., 1926, 589). The other possibility is that the blood-red coloration is due to the transient formation of the free aurous radicals, R·SAu<, which polymerise to form the pale yellow auromercaptides R·SAu:AuS·R or, in general, $(R{\cdot}S{\cdot}Au<)_n$. The properties of these auromercaptides are in agreement with this formulation : they are all amorphous substances with well-marked colloidal properties.

In the reaction of only one other reducing agent with auric solutions have we observed a transient red coloration. In the preparation of sodium gold thiosulphate, $Na_3Au(S_2O_3)_2$, by the action of a neutral solution of gold chloride on sodium thiosulphate, a transient red colour is obtained which, examined spectroscopically, has a similar general absorption in the visible region to the blood-red colour obtained with thiolglyoxalines. In this case also, the reaction is essentially a reduction to the aurous state. Brown's view (*J. Amer. Chem. Soc.*, 1927, **49**, 959) that the colour is due to the formation of sodium aurate does not tally with the colour of alkali aurates, which are pale yellow or pale green.

2-Aurothiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylic acid (VI) prepared as described above invariably contains an excess of combined gold in the approximate ratio of N:Au = 2 : 1·08 which finds a ready interpretation by analogy with the arsenicals. Just as over-reduction of arsinic acids leads to production of polyarsenides, which are usually formulated as in (VII), so here the product probably contains (VIII).

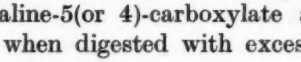
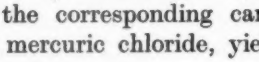
(VII.)




(VIII.)

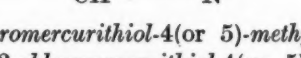
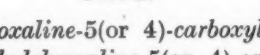
The reaction of thiolglyoxalines with mercuric salts is in striking contrast to their behaviour towards auric chloride. When ethyl glyoxaline-4(or 5)-carboxylate is digested in alcoholic solution with mercuric acetate, it yields *ethyl* 1-*acetoxymercuriglyoxaline*-4(or 5)-

carboxylate (IX) quantitatively, but ethyl 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylate and the corresponding carboxylic acid, when digested with excess of mercuric chloride, yield *ethyl*

(IX.)   (X.)

2-*chloromercurithiol*-4(or 5)-*methylglyoxaline*-5(or 4)-*carboxylate* (X) and 2-*chloromercurithiol*-4(or 5)-*methylglyoxaline*-5(or 4)-*carboxylic acid* (XI) respectively. These are crystalline compounds and their constitution follows from their behaviour towards sodium hydroxide and ammonium sulphide.

Results of considerable interest have been obtained in an attempt to prepare the disulphide (XII) which should have arisen in the action of auric chloride on 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylic acid (V). It cannot be obtained by oxidation of the corresponding thiol acid by iodine, as partial replacement of the

(XI.)   (XII.)

carboxyl group by iodine takes place, and it is not formed when 4(or 5)-*carbethoxy*-5(or 4)-*methylglyoxaline*-2-*disulphide* (XIII), prepared by the action of iodine upon ethyl 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylate, is hydrolysed by alkalis or acids. After this ester disulphide (XIII) had been boiled for an hour with 10% aqueous sodium carbonate, the products isolated were 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylic acid (V), the corresponding decarboxylated product 2-thiol-4(or 5)-methylglyoxaline, ethyl 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylate (III), and sulphur dioxide. On acid hydrolysis, 2-thiol-4(or 5)-methylglyoxaline was also obtained with other substances. Quantitative estimation of the sulphur dioxide produced showed that 74% of that required by the equation $2RS{\cdot}SR + 2H_2O = 3R{\cdot}SH + RH + SO_2$ was present. The mother-liquor contained sulphate, so that the deficiency in sulphur dioxide is probably accounted for by the reducing action of sodium sulphite on the disulphide, for the disulphide (XIII) is readily reduced to the thiol ester in aqueous solution by sulphur dioxide.

It seems probable that an unstable sulphinic acid is the intermediate product in the above hydrolysis, in which case the reaction would be the reverse of the mode of synthesis of disulphides of Otto and Schiller (*Ber.*, 1876, **9**, 1589):

$$3R{\cdot}SH + R{\cdot}SO_2H = 2RS{\cdot}SR + 2H_2O.$$

In support of this view, the first sulphinic acid in the glyoxaline series has been prepared and proves to be a very unstable substance

readily yielding sulphur dioxide at room temperature. When 2-thiol-4(or 5)-methylglyoxaline (XIV) is added at 0° to 10% hydrogen peroxide (2 mols.), it is converted for the most part into 4(or 5)-*methylglyoxaline-2-sulphinic acid* (XV) with simultaneous formation of small quantities of 4(or 5)-*methylglyoxaline-2-sulphonic acid* (XVI), 4(or 5)-methylglyoxaline, and sulphuric acid.

(XIII.) $\left(\begin{array}{l}EtO_2C\cdot C\!-\!NH\\ \quad\|\quad\ \ \diagdown\\ \quad CMe\cdot N\end{array}\!\!>C\cdot S-\right)_2$ $\begin{array}{l}CMe\cdot NH\\ \|\quad\ \diagdown\\ CH\!-\!N\end{array}\!\!>C\cdot SH$ (XIV.)

(XV.) $\begin{array}{l}CMe\cdot NH\\ \|\quad\ \diagdown\\ CH\!-\!N\end{array}\!\!>C\cdot SO_2H$ $\begin{array}{l}CMe\cdot NH\\ \|\quad\ \diagdown\\ CH\!-\!N\end{array}\!\!>C\cdot SO_3H$ (XVI.)

The sulphinic acid is a crystalline solid, stable at 0°. It has an acid reaction, but at room temperature it changes after a few hours into a strongly basic liquid containing 4(or 5)-methylglyoxaline and its *sulphite*. It consumes one atom of oxygen when titrated with permanganate at 0°, and is converted by excess of hydrogen peroxide, preferably in the presence of alkali, into the sulphonic acid. The formation of this unstable sulphinic acid is, in fact, exactly analogous to the formation of the somewhat more stable aminoiminomethanesulphinic acid, $NH{:}C(NH_2)\cdot SO_2H$, by the oxidation at 0° of thiocarbamide by hydrogen peroxide (Barnett, J., 1910, **97**, 63).

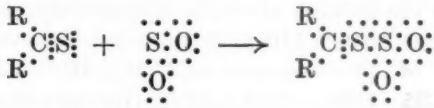
The instability of the glyoxalinesulphinic acid affords a satisfactory interpretation of the desulphuration of 2-thiolglyoxalines by means of nitric acid discovered by Wohl and Marckwald (*Ber.*, 1889, **22**, 575). These authors postulated the formation of an unstable sulphonic acid which was hydrolysed even under the conditions of oxidation :

$$N{:}C(SH)\cdot NH^- \longrightarrow -N{:}C(SO_3H)\cdot NH^- \longrightarrow -N{:}CH\cdot NH^- + H_2SO_4.$$

This explanation was, however, disproved by the observations of Anschütz and Schwickerath (*Annalen*, 1895, **284**, 9), Biltz and Krebs (*ibid.*, 1912, **391**, 203), and Lamb and Pyman (J., 1924, **125**, 707). Biltz and Krebs favoured the view that disulphides are the intermediate products, but the results are much more compatible with the view that an unstable sulphinic acid is formed, and the more unstable it is, the smaller the proportion of sulphonic acid formed in the oxidation and the larger the proportion of desulphurised glyoxaline.

When the alkaline hydrolysate of 4(or 5)-carbethoxy-5(or 4)-methylglyoxaline-2-disulphide (XIII) is acidified to Congo-paper, the solution turns yellow and evolves sulphur dioxide. On removal of this by aspiration, the yellow colour vanishes, but it is restored when sulphur dioxide is passed into the solution. This has been traced to the formation of unstable, yellow or orange-yellow addition

compounds between many 2-thiolglyoxalines and sulphur dioxide in aqueous or acid solution or in the dry state. Quantitative measurement of the amount of sulphur dioxide absorbed by dry 2-thiol-1-phenylglyoxaline showed that exactly one molecule is absorbed under one atmosphere of sulphur dioxide, but on exposure to the air the compound has a half-life period of 10 minutes. The reaction is also given by thiocarbamide, and is strikingly shown by allylthiocarbamide and 2-thiol-1 : 4-dimethylglyoxaline, which are immediately converted into yellow and orange-yellow liquids, respectively, by exposure to sulphur dioxide. The constitution of these labile addition compounds is best interpreted as a simple addition of the sulphur atom of the thiol group to the electromeric modification of sulphur dioxide containing two semi-polar double bonds.



This interpretation does not discriminate between the –NH·C(SH):N– structure and the –NH·CS·NH– structure of 2-thiolglyoxalines. Korczyński and Glebocka (*Gazzetta*, 1920, **50**, i, 378) have described a number of addition compounds of sulphur dioxide with a variety of amines, including thiocarbamide, and attribute their formation to the secondary valencies of the nitrogen atom. Ethyl 4(or 5)-glyoxalinecarboxylate, however, does not add on sulphur dioxide, so that their interpretation does not hold here.

The similarity between thiocarbamides and 2-thiolglyoxalines in their behaviour towards sulphur dioxide extends to the colour reaction described by Sato (*Biochem. Z.*, 1909, **23**, 45) for thiocarbamides, and an improved form of the test is described in the experimental portion together with a number of other colour reactions which may prove of service in this field.

In order to characterise 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylic acid (V) more fully, it has been converted by esterification by alcoholic hydrogen chloride (compare Burtles, Pyman, and Roylance, J., 1925, **127**, 588) into *ethyl 2-ethylthiol*-4(or 5)-*methylglyoxaline*-5(or 4)-*carboxylate* (XVII), which on hydrolysis yields *2-ethylthiol*-4(or 5)-*methylglyoxaline*-5(or 4)-*carboxylic acid* (XVIII) and its decarboxylation product, *2-ethylthiol*-4(or 5)-*methylglyoxaline*.

(XVII.) $EtO_2C\cdot C(=CMe\cdot N)\!-\!NH\!>\!C\cdot SEt$ $\qquad$ $CO_2H\cdot C(=CMe\cdot N)\!-\!NH\!>\!C\cdot SEt$ (XVIII.)

The acid (XVIII) forms a *monohydrochloride* and a *semihydrochloride* and thus resembles some of the amino-acids, such as glycine and *dl*-alanine, which form normal and semi-hydrochlorides,

and the many anomalous amine salts recorded by Werner (*Ber.*, 1903, **36**, 149). The majority of these were formulated by Werner in terms of co-ordinated hydrogen: $XH + 2NR_3 = X{\cdot}H\begin{matrix}NR_3\\ \\ NR_3\end{matrix}$, which on the electronic theory of valency would be readily interpreted as

$$XH + 2R{:}\overset{\displaystyle R}{\underset{\displaystyle R}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}}}{:} = \left[\begin{matrix} & R & & R & \\ R{:} & \overset{\cdot\cdot}{\underset{\cdot\cdot}{N}} & {:}H{:} & \overset{\cdot\cdot}{\underset{\cdot\cdot}{N}} & {:}R \\ & R & & R & \end{matrix}\right]^{+} X^{-}.$$

The case is in fact the parallel of the interpretation put forward for potassium hydrogen fluoride, KHF_2, where, however, co-ordinated hydrogen links the fluorine atoms in a negatively charged complex (Lewis, " Valence," 1923, 110). A difficulty, however, arises in the interpretation of the compounds $(NH_3)_4$,HCl (Joannis, *Compt. rend.*, 1902, **135**, 1106), $(NH_3)_4$,HBr (Bakhuis-Roozeboom, *Rec. trav. chim.*, 1885, **4**, 361), and $(NH_3)_4$,HNO_3 (Kuriloff, *Z. physikal. Chem.*, 1898, **25**, 108). These would indicate a co-ordination number of 4 for hydrogen or else chain formation of ammonia molecules with links of co-ordinated hydrogen.

We are indebted to Captain S. R. Douglas, F.R.S., for a determination of the effect of sodium aurothiolmethylglyoxalinecarboxylate on tubercle bacilli. It inhibits the growth of these organisms *in vitro* at a dilution of 1 in 100,000 (not tested at lower concentrations). Guinea-pigs were injected each with 0·5 mg. of a virulent culture of tubercle bacilli which had been subjected for 12 hours to a concentration of the sodium salt ranging from 1 in 1,000,000 to 1 in 1000. The time elapsing between injection and death of the animal from tuberculosis was progressively longer with increasing concentration of the salt used in the preliminary treatment of the bacilli. In no case had sterilisation been effected. Rabbits inoculated with a virulent strain were injected weekly with the sodium salt (0·01 g. per kilo.) and after four injections the lungs showed less signs of tubercular lesions than the controls, whilst the death of mice inoculated with the bacilli was distinctly delayed by one and by two injections of the sodium salt, 50 mice being used as controls, 25 mice for one dose and 25 for two doses.

To Miss Durham and Miss Marchal we are indebted for a determination of the toxicities to mice of sodium aurothiolmethylglyoxalinecarboxylate (0·05 mg. per g.) and of sodium 2-chloromercurithiolmethylglyoxalinecarboxylate (0·005 mg. per g.). The same compounds were tested for curative action on mice infected with trypanosomes, but no such action was detected.

Our thanks are also due to Professor F. L. Pyman, F.R.S., for the gift of samples of a series of thiolglyoxalines from his unique collection.

EXPERIMENTAL.

Hydrolysis of Ethyl 2-Thiol-4(or 5)-*methylglyoxaline-5*(or 4)-*carboxylate* (III).—This ester was prepared in 42% yield from ethyl acetoacetate as described by Posner and Gabriel (*Ber.*, 1894, **27**, 1141), but Wolff's method (*Annalen*, 1902, **325**, 135) was used for the preparation of oximinoacetoacetic ester. It melts at 236—237° (P. and G. give 229°) and is soluble in 64 parts of boiling water.

The ester (50 g.) was boiled for 1 hour with 100 g. of sodium carbonate (anhydrous) in 1000 c.c. of water, and the reaction then adjusted to neutrality to Congo-paper. The precipitate and the successive crops obtained by evaporation of the mother-liquors (in all, 38·3 g.) were extracted with one-half saturated sodium hydrogen carbonate solution, which removed the whole of the carboxylic acid and the major portion of the decarboxylated base, leaving behind non-hydrolysed ester mixed with a little decarboxylated base. The main alkaline extract on neutralisation to Congo-paper gave the carboxylic acid (23·35 g.), and the mother-liquors on concentration gave the thiol base (3·7 g.). The portion insoluble in sodium hydrogen carbonate solution (9·05 g.) was boiled with water (50 c.c.) and left, undissolved, almost pure ester (3·5 g.); the water-soluble fraction was made alkaline with sodium carbonate and boiled down in an open flask to hydrolyse the ester still present. From this alkaline liquor the thiol base was recovered in successive crops, 6·0 g. in all, the mother-liquors which gave the thiol base (3·7 g.) being incorporated at one stage. The final liquor was acidified to Congo-paper and gave a small crop of carboxylic acid (0·4 g.).

2-*Thiol*-4(or 5)-*methylglyoxaline*-5(or 4)-*carboxylic acid* (V) is soluble in 100 parts of boiling water and separates in granular crystals. It melts with loss of carbon dioxide at 240—241°, and the crystalline residue obtained, at 244—245°, the m. p. of 2-thiol-4(5)-methylglyoxaline (Found: S, 20·5; N, 17·9. $C_5H_6O_2N_2S$ requires S, 20·3; N, 17·2%). The acid gives an immediate red colour with Pauly's reagent in sodium carbonate solution.

Esterification of 2-Thiol-4(or 5)-*methylglyoxaline*-5(or 4)-*carboxylic Acid.*—The acid (5 g.) was suspended in 100 c.c. of absolute alcohol, and the liquid saturated with hydrogen chloride at 0°. The suspension was then boiled for 3 hours with further passage of the gas. After removal of alcohol and excess of acid by evaporation with water, the syrupy residue was dissolved in 20 c.c. of water and treated with saturated potassium carbonate solution so long as a crystalline precipitate separated. This amounted to 4·4 g., and

when crystallised from the minimum volume (350 c.c.) of boiling water separated in long, white, silky needles (4·05 g.), m. p. 144—145°.

Ethyl 2-ethylthiol-4(or 5)-*methylglyoxaline-5*(or 4)-*carboxylate* (XVII) is readily soluble in boiling organic solvents, but crystallises conveniently only from acetone, ethyl acetate, or water (Found in air-dried material : loss at 100°, 10·7. $C_7H_{10}O_2N_2S,1\frac{1}{2}H_2O$ requires H_2O, 11·2%. Found in anhydrous solid : N, 12·8. $C_7H_{10}O_2N_2S$ requires N, 13·1%). It forms very soluble salts with nitric, hydrochloric and sulphuric acids, the *hydrochloride* crystallising in needles. It forms an oily *chloroaurate*, but a *picrate* crystallising in glistening, yellow prisms, m. p. 135—136° (Found : picric acid by nitron, 52·1. $C_9H_{14}O_2N_2S,C_6H_3O_7N_3$ requires picric acid, 51·7%).

In a preliminary experiment (1·6 g. of thiol acid) where esterification was only carried out for 90 minutes, the product precipitated at neutrality (1·35 g.) gave by ether extraction 1·25 g. of *S*-ethyl ether and 0·1 g. of insoluble material which proved to be ethyl 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylate.

S-*Alkylation of Ethyl 2-Thiol-4*(or 5)-*methylglyoxaline-5*(or 4)-*carboxylate*.—The 2-thiolcarboxylic ester (10 g.) was suspended in 100 c.c. of absolute alcohol and submitted to the same treatment as in the foregoing esterification. The yield of crude *S*-ethyl ether was 10·8 g. It was recrystallised from 100 volumes of boiling water and gave 10·3 g. of pure material crystallising in needles, m. p. 144—145°. On prolonged standing, the mother-liquor deposited stout, triangular plates which proved to be the same substance, m. p. 143—144°.

Alkaline Hydrolysis of Ethyl 2-Ethylthiol-4(or 5)-*methylglyoxaline-5*(or 4)-*carboxylate*.—The ethyl ester of the *S*-ethyl ether (8·1 g.) was boiled for 4 hours with 16·2 g. of anhydrous sodium carbonate in 162 c.c. of water. The ethereal extract on evaporation gave 2·3 g. of *2-ethylthiol-4*(or 5)-*methylglyoxaline*, m. p. 68—69°. This base was insoluble in light petroleum and very soluble in benzene, and crystallised well from ethyl ether in delicate, rectangular leaflets, m. p. 69—71°. It was converted into the *picrate* (5·5 g.), which was soluble to the extent of 2·3% in boiling water and separated on cooling in prismatic needles, m. p. 136—137° (Found : picric acid by nitron, 62·6, 62·7. $C_6H_{10}N_2S,C_6H_3O_7N_3$ requires picric acid, 61·7%). The picrate was converted into the hydrochloride, which could not be crystallised, and a portion of the latter precipitated with chloroauric acid. The *chloroaurate* separated in red plates, m. p. 130—131° without decomposition (Found : Au, 41·0. $C_6H_{10}N_2S,HAuCl_4$ requires Au, 40·9%).

The alkaline liquors after ethereal extraction were made very

faintly acid to Congo-paper and concentrated; two crops of needles, 4·05 g. in all, were then obtained. Of this, 3·3 g. were dissolved in 10 c.c. of boiling water in a covered vessel to avoid access of nuclei from the air. When the solution was cool and supersaturated, it was inoculated with nuclei of the needles. The crop of needles (2·3 g.) was collected and washed with ice-cold water [Found: Cl, 8·3; N, 13·4. $(C_7H_{10}O_2N_2S)_2$,HCl requires Cl, 8·7; N, 13·7%]. This *semihydrochloride* of 2-*ethylthiol*-4(or 5)-*methylglyoxaline*-5(or 4)-*carboxylic acid* was very readily soluble in water, with a reaction faintly acid to Congo-paper. It melted rather indefinitely with effervescence between 122° and 125°, but without loss of carbon dioxide, as the residue did not give a picrate. If a strong aqueous solution was heated, the free *carboxylic acid* (XVIII) separated in stout rhombs; on cooling, needles of the semi-hydrochloride invariably separated, but the rhombs, even on prolonged standing, remained unchanged. If alkali was added until the faint acidity to Congo-paper was completely removed and the reaction was very faintly acid to sensitive methyl-orange paper, the free carboxylic acid was precipitated. It was soluble in 10 parts of boiling water and crystallised in large, rectangular tablets, m. p. 179—180° (efferv.) (Found: N, 14·9. $C_7H_{10}O_2N_2S$ requires N, 15·0%). The decarboxylated melt solidified and melted at 67° and gave a picrate identical with 2-ethylthiol-4(or 5)-methylglyoxaline picrate.

If the semi-hydrochloride (0·2 g.) be dissolved in a few drops of hot 3*N*-hydrochloric acid it forms a syrupy solution which soon deposits large, triangular prisms of the *monohydrochloride*, m. p. 189—190° (efferv.) (Found: Loss at 100°, 7·8. $C_7H_{10}O_2N_2S$,HCl,H_2O requires H_2O, 7·5%. Found in dried salt: Cl, 16·0. $C_7H_{10}O_2N_2S$,HCl requires Cl, 15·9%). This salt is very soluble in water, the solution turning Congo-paper blue.

Preparation of 5(or 4)-*Carbethoxy*-4-(or 5)-*methyl*-2-*glyoxaline Disulphide* (XIII).—Ethyl 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylate (1 g.) was dissolved in 1000 c.c. of hot water, cooled to 50°, and treated with *N*/10-iodine solution until a slight excess was present as shown by the pale brown colour. Usually 55 c.c. were required instead of the theoretical 53·7 c.c. Three further batches were treated similarly. The *disulphide* (3·25 g.) which separated during the addition of iodine was collected; the mother-liquors, on being again treated with iodine until present in slight excess, and then neutralised with sodium carbonate, deposited a further 0·2 g. of disulphide. The product (yield, 86%), m. p. 220—222°, separated from boiling alcohol (120 c.c.) as a voluminous felt of pale yellow needles; after a further crystallisation, the m. p. was con-

stant at 222—223° (yield, 3·25 g.) (Found : N, 15·3. $C_{14}H_{18}O_4N_4S_2$ requires N, 15·1%). The same ester with the same m. p. was obtained by oxidation of the thiol ester in alkaline solution with potassium ferricyanide, but it was difficult to free it from Prussian blue, formed in traces. It was also obtained by dissolving the thiol ester in spirit, adding a lump of fused sodium nitrite, and running *N*-sulphuric acid on to the nitrite so that there was a vigorous evolution of gases through the liquid. The solution eventually deposited the disulphide. A modification of this method may prove to be the most accessible route to this disulphide. In sodium carbonate solution, the disulphide gives a yellow colour with Pauly's reagent. The ester is readily reduced to the thiol ester by passage of sulphur dioxide in aqueous solution.

Hydrolysis of the Disulphide.—(a) *By alkali.* The disulphide (7·4 g.) was boiled for 1 hour with 15 g. of anhydrous sodium carbonate in 150 c.c. of water. The solution, on being neutralised to Congo-paper, turned yellow, evolved sulphur dioxide, and gave a fraction (2·95 g.). On concentration, two further fractions (0·45 and 1·6 g.) were obtained. The sodium hydrogen carbonate extracts of these fractions gave, on neutralisation to Congo-paper, 2·76 g. of 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylic acid, identical in all its reactions with the product of hydrolysis of the corresponding 2-thiol ester. The portion soluble in sodium hydrogen carbonate but not precipitated on neutralisation was isolated by concentration and proved to be pure 2-thiol-4(or 5)-methylglyoxaline (0·1 g.), m. p. 244—245°. The portion of original material insoluble in sodium hydrogen carbonate, on three crystallisations from water, gave 0·4 g. of ethyl 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylate, m. p. 237°.

Quantitative determinations of the proportion of sulphur dioxide formed in the hydrolysis of the disulphide were made by hydrolysing 1·23 g. (*M*/300) with 2·46 g. of anhydrous sodium carbonate in 24·6 c.c. of water for 1 hour at 100°. The alcoholic distillate contained only a trace of reducing substance, possibly acetaldehyde. The alkaline mother-liquor was made acid by addition of 3*N*-hydrochloric acid, and the liberated sulphur dioxide absorbed by aspiration into standard *N*/10-iodine solution, any volatile iodine being caught in *N*/10-sodium thiosulphate solution. In two separate experiments, 72·4 and 73·5% of the sulphur dioxide required by the equation $2RS{\cdot}SR + 2H_2O = SO_2 + RH + 3RSH$ was found. The mother-liquors also contained appreciable amounts of sulphate. The method of estimation was controlled by experiments on standard sodium sulphite solution and found to agree within 2%.

(b) *By acid.* The disulphide (0·9 g.) was boiled for 3 hours with

10 c.c. of 16% hydrochloric acid. The solution was evaporated dry at 50°, and the residue was dissolved in a little water and made faintly alkaline to litmus; an amorphous base (0·4 g.) then separated. This was probably a mixture of bases, as it did not behave normally on reduction to the thiol base with sulphur dioxide or on oxidation to a base free from sulphur by dilute nitric acid. After removal of the amorphous substance, the mother-liquors, on concentration, gave 0·2 g. of crude 2-thiol-4(or 5)-methylglyoxaline, m. p. 239°. Recrystallised from 1·2 c.c. of hot water, it separated in the characteristic large crystals of the pure thiol base, m. p. 244°.

*Preparation of Ethyl 2-Aurothiol-*4(or 5)-*methylglyoxaline-*5(or 4)-*carboxylate* (IV).—Ethyl 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylate (1·86 g.; 3 mols.) in 100 c.c. of dry methyl alcohol was treated with 1 g. (1 mol.) of gold trichloride in 30 c.c. of methyl alcohol. The solution became brilliant ruby-red and after 2 hours was pale yellow. The alcohol was removed and treatment of the residue with 400 c.c. of boiling water left 0·22 g., m. p. 254° (decomp.), undissolved. On keeping, the solution deposited needles (1·35 g.), m. p. 170°, containing 30·3% of combined gold. These were extracted with a further 150 c.c. of boiling water, which left 0·35 g. of solid undissolved, m. p. 252° (decomp.). This was the required *ethyl* 2-*aurothiol-*4(or 5)-*methylglyoxaline-*5(or 4)-*carboxylate* (Found: Au, 50·6. $C_7H_9O_2N_2SAu$ requires Au, 51·6%). Attempts to convert this ester into the corresponding acid by hydrolysis led to decomposition with separation of gold.

Preparation of 2-*Aurothiol-*4(or 5)-*methylglyoxaline-*5(or 4)-*carboxylic Acid* (VI).—2-Thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylic acid (4·7 g.), dissolved in 435 c.c. of pure dry methyl alcohol, was treated with 3·0 g. (1/3 mol.) of gold trichloride in 10 c.c. of methyl alcohol. After 1 hour, the deep ruby-red colour which developed immediately on mixing had completely gone. The yellow solution was concentrated to about 10 c.c. and diluted with 250 c.c. of water. The solution set to a jelly which rapidly broke up with deposition of a mixture of amorphous and crystalline matter. There was no free gold present. The solid was collected, and dissolved in 100 c.c. of water with the aid of 22 c.c. of saturated sodium hydrogen carbonate solution. Addition of 30 g. of sodium chloride caused the separation of a white, amorphous precipitate of the sodium salt of the crude aurothiol acid. It was redissolved in 100 c.c. of water, by gentle warming with addition of a few drops of 2*N*-sodium hydroxide, and reprecipitated by 30 g. of sodium chloride. This process was repeated in order to eliminate the last traces of thiol acid. The amorphous sodium salt was suspended in water and treated with excess of 3*N*-hydrochloric acid, and the

amorphous aurothiol acid was centrifuged off, resuspended in water, and re-centrifuged so long as the supernatant fluid showed chloridion. The acid, after being dried in a vacuum and ground, was obtained as a pale primrose-yellow powder (yield, 2·7 g. or 77%) (Found : Loss on prolonged drying at 110°, 6·3%. Found in anhydrous solid : N, 7·6; Au, 57·8, 57·8. $C_5H_5O_2N_2SAu$ requires N, 7·9; Au, 55·6%). On ignition even with nitric and sulphuric acids, this aurothiol acid leaves a residue of gold soluble in cold aqua regia but containing a small quantity of insoluble black material. This is destroyed by digestion with hot aqua regia, and after removal of nitric acid the gold can be quantitatively precipitated by excess of ferrous chloride in acid solution. If insufficient acid be added, the gold contains a large quantity of iron (compare Treadwell, " Analytische Chemie," 1921, II, 213).

The aurothiol acid forms a clear pale yellow solution on neutralisation with sodium hydrogen carbonate and can be boiled without decomposition.

The first two sodium chloride precipitation liquors of the sodium salt, on acidification to Congo-paper, gave precipitates of 1·37 g. and 0·1 g., respectively, of crystalline 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylic acid. This was identical in all its reactions with the 2-thiol acid prepared by hydrolysis of its ethyl ester. In particular, 1·2 g. were esterified by alcoholic hydrogen chloride and gave 1·1 g. of ethyl 2-ethylthiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylate.

In some experiments, the salting-out of the amorphous sodium salt of the aurothiol acid led to simultaneous separation of flattened needles of the sodium salt of the 2-thiol acid. This could be eliminated only by increasing the number of precipitations.

Action of Mercuric Acetate on Ethyl Glyoxaline-4(or 5)-*carboxylate.*—Ethyl glyoxalinecarboxylate (0·7 g.) was dissolved in 25 c.c. of alcohol and treated with 1·6 g. (1 mol.) of mercuric acetate. The gelatinous mass immediately produced was boiled for 6 hours; it then consisted of homogeneous, microscopic, flat prisms almost insoluble in cold alcohol (yield, 2·0 g.). *Ethyl* 1-*acetoxymercuriglyoxaline*-4(5 ?)-*carboxylate* (IX) is instantly soluble in dilute hydrochloric acid, and black mercuric sulphide is precipitated from the solution by hydrogen sulphide. Sodium hydroxide produces orange-yellow mercuric oxide. The ester has no definite melting point, but shrinks suddenly at about 222° and is not further changed at 300° (Found : Loss at 100°, 2·8. $C_8H_{10}O_4N_2Hg,\frac{1}{2}H_2O$ requires H_2O, 2·2%. Found in dried substance : N, 6·8; Hg, 50·8. $C_8H_{10}O_4N_2Hg$ requires N, 7·0; Hg, 50·4%).

Action of Mercuric Chloride on Ethyl 2-*Thiol*-4(or 5)-*methylglyoxaline*-5(or 4)-*carboxylate.*—The thiol ester (1·86 g.) was boiled

with 5·4 g. (2 mols.) of mercuric chloride in 50 c.c. of absolute alcohol for 6 hours. On standing for a few days, *ethyl 2-chloromercurithiol-4*(or 5)-*methylglyoxaline-5*(or 4)-*carboxylate* (X), m. p. 167—168°, separated in six-sided plates (yield, 95%). It was soluble without difficulty in 3 volumes of boiling absolute alcohol (Found: N, 6·5. $C_7H_9O_2N_2ClSHg$ requires N, 6·7%). The ester does not give mercuric oxide on treatment with sodium hydroxide, but is immediately blackened by ammonium sulphide.

Action of Mercuric Chloride on 2-Thiol-4(or 5)-*methylglyoxaline-5*(or 4)-*carboxylic Acid.*—The thiol acid (1·58 g.), dissolved in 100 c.c. of pure dry methyl alcohol, was boiled for 6 hours with 5·43 g. (2 mols.) of mercuric chloride. After remaining for 12 hours at room temperature, the solution deposited 0·25 g. of substance, and on concentration a further 0·8 g. *2-Chloromercurithiol-4*(or 5)-*methylglyoxaline-5*(or 4)-*carboxylic acid* (XI), m. p. 257° (efferv.), is readily soluble in sodium hydrogen carbonate solution and is precipitated unchanged, but microcrystalline, on addition of hydrochloric acid (Found: N, 7·1. $C_5H_5O_2N_2ClSHg$ requires N, 7·1%). Mercuric sulphide is readily precipitated when hydrogen sulphide is passed into a suspension of the acid in hot dilute mineral acid solution, or instantly by the action of ammonium sulphide. The acid does not give mercuric oxide on treatment with sodium hydroxide.

Action of Hydrogen Peroxide on 2-Thiol-4(or 5)-*methylglyoxaline.*—Finely powdered thiolmethylglyoxaline (1·14 g.) was added in portions to a stirred solution of 2·4 g. (2 mols.) of Merck's perhydrol in 6 c.c. of water at 0° to −5°. The thiol compound rapidly passed into solution through oxidation and yielded a clear solution which after a short time became filled with microscopic leaflets of 4(or 5)-*methylglyoxaline-2-sulphinic acid* (XV). These were filtered off on an ice-jacketed funnel at 0° and washed with ice-cold water (yield, about 0·7 g.). For analysis, portions were removed, rubbed quickly on ice-cold porous plate, and rapidly weighed (Found: N, by Kjeldahl's method, 15·7; SO_2 evolved by digestion with boiling dilute sulphuric acid and absorbed by aspiration in *N*/10-iodine, 36·7; N in distillation residue, by Kjeldahl's method, 15·9—whence $SO_2 : N = 1·01 : 2$. $C_4H_6O_2N_2S,2H_2O$ requires SO_2, 35·2; N, 15·4%. Found: oxygen consumed by oxidation with *N*/10-permanganate in 2*N*-sulphuric acid at 0°, 8·1. $C_4H_6O_2N_2S,2H_2O$ requires O, 8·8%). This sulphinic acid is an unstable substance. When kept for a few hours either in a vacuum over sulphuric acid or in the air at room temperature, it passes into a clear basic liquid with loss of some sulphur dioxide. This liquid residue, when kept dry or when heated on the water-bath, partly crystallises as the normal *sulphite* of 4-methylglyoxaline. If the basic residue be

mixed with saturated potassium carbonate solution and extracted with chloroform, the latter on evaporation yields a base which readily crystallises completely as 4-methylglyoxaline. The sulphinic acid melts at 73° and effervesces at 92°. It is faintly acid to sensitive methyl-orange paper and dissolves in sodium hydrogen carbonate solution with evolution of carbon dioxide. It is not very readily soluble in ice-cold water and gives no precipitate with ferric chloride. Its ammoniacal solution gives no precipitate with calcium or barium chloride.

The mother-liquors of the oxidation were evaporated to a small volume over sulphuric acid in a desiccator and then deposited clusters of fine needles (0·1 g.) of the corresponding sulphonic acid (see below). The mother-liquor also contained sulphate and 4-methylglyoxaline, the latter being readily removed from saturated potassium carbonate solution by chloroform.

4(or 5)-*Methylglyoxaline-2-sulphonic Acid* (XVI).—2-Thiol-4(or 5)-methylglyoxaline (0·57 g.) was oxidised by hydrogen peroxide (3 mols.) in the way described in the previous section. When the sulphinic acid had crystallised from the liquor, 2*N*-sodium hydroxide (2 c.c.) was added drop by drop until an alkaline reaction was attained. The clear solution was concentrated at room temperature over sulphuric acid in a vacuum for 12 hours and had then become acid (decomposition of sulphinic acid) in reaction with deposition of a few crystals of the sulphonic acid. It was made acid to Congo-paper and gradually deposited the sulphonic acid (yield 0·55 g.). For analysis, 0·35 g. was dissolved in 0·2 c.c. of hot water and gave 0·3 g., crystallising in stout columns, m. p. about 280° (Found: Loss at 100°, 10·3. $C_4H_6O_3N_2S,H_2O$ requires H_2O, 10·0%. Found in dried substance: N, 16·9. $C_4H_6O_3N_2S$ requires N, 17·2%). This sulphonic acid is faintly acid to Congo-paper and methyl-orange paper and is stable to acid permanganate. The *calcium* and *barium* salts are very soluble in water. The *ammonium* salt is readily soluble, but crystallises well in microscopic rods.

Action of Sulphur Dioxide on 2-Thiolglyoxalines.—If 2-thiol-4(or 5)-methylglyoxaline, ethyl 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylate or 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylic acid be dissolved in *N*-hydrochloric acid and subjected to a current of sulphur dioxide, the solution immediately becomes yellow. The same behaviour is shown by thiocarbamide but not by cysteine. When 2-thiol-1-phenylglyoxaline, 2-thiol-1-phenyl-4-methylglyoxaline, 2-thiol-1 : 5-dimethylglyoxaline, and 2-thiol-1 : 4-dimethylglyoxaline are dissolved in water and saturated with sulphur dioxide, yellow solutions are produced and in the case of the two 1-phenyl derivatives orange-yellow crystalline addition

products separate readily. These are stable in presence of excess of sulphur dioxide, but redissolve as the sulphur dioxide passes off. 2-Thiol-4 : 5-diphenylglyoxaline, unlike all the other 2-thiolglyoxalines examined, showed no visible change, possibly owing to its sparing solubility in water. When sulphur dioxide is passed over powdered 2-thiolglyoxalines, they become yellow to orange-yellow through absorption of the gas. Thus 2-thiol-1-phenyl-, 2-thiol-1-phenyl-4-methyl-, 2-thiol-1 : 5-dimethyl-, 2-thiol-4-methyl-, and 5-carbethoxy-2-thiol-4-methyl-glyoxalines all become yellow on exposure to sulphur dioxide. Thiocarbamide became pale yellow, but 2-thiol-1 : 4-dimethylglyoxaline and allylthiocarbamide (thiosinamine) immediately liquefied on exposure to the gas, forming orange and yellow liquids respectively. 5-Carbethoxy-4-methyl-2-glyoxaline disulphide went deeper yellow on exposure to the gas and in aqueous suspension was rapidly reduced to the corresponding thiol compound. The hydrated form of ergothioneine from blood was immediately converted into an orange-coloured, pasty product by exposure to sulphur dioxide.

Quantitative Absorption Experiments.—Finely divided 2-thiol-1-phenylglyoxaline (0·0712 g.) was submitted to a current of sulphur dioxide in a small U-tube fitted with pierced ground glass stoppers and side arms. Absorption of the gas was rapid and at the end of 2 hours 0·0249 g. had been absorbed. From this point absorption was slow and after 12 hours the total absorption was 0·0263 g., corresponding to 1·01 molecule of sulphur dioxide. When this compound was exposed to the air in an open boat, it was one-half dissociated in 10 minutes. In a similar manner, thiocarbamide (0·1211 g.) absorbed 0·74 molecule of sulphur dioxide in 15 hours, becoming pale yellow; absorption thereafter was very slow. Korczyński and Glebocka (*loc. cit.*) found absorption of 0·5 mol. and described their product as white. In the former case, after the sulphur dioxide had completely gone, the m. p. of the original substance was unchanged. In the latter case, there was a slight depression. A control experiment on ethyl 4(or 5)-glyoxaline-carboxylate showed negligible absorption of sulphur dioxide.

Colour Reactions for Thiolglyoxalines.—The colour reactions of thiolglyoxalines with sulphur dioxide and with auric chloride have been described above. Sato's reaction for thiocarbamide (*loc. cit.*) is applicable to thiolglyoxalines and is best carried out as follows : The substance is dissolved in water, treated with one drop of glacial acetic acid followed by one drop of potassium ferrocyanide solution; a yellowish-green solution is then produced which on warming rapidly becomes intense blue. Tschugaev's reaction (*Ber.*, 1902, **35**, 2483) for thiocarbamide, an intense gentian-blue on warming

with benzophenonechloride, although given by allylthiocarbamide, is not given by 2-thiolglyoxalines. Rheinboldt's reaction for thiol groups (*Ber.*, 1927, **60**, 184)—a wine-red solution—does not apply to 2-thiolglyoxalines or thiocarbamides, which all give yellow solutions. Tanret (*Compt. rend.*, 1909, **149**, 222) described a colour reaction for ergothioneine, which, on warming with chloroform and potassium hydroxide solution, gave a green solution which became blue on acidification. This reaction has been tried on a wide variety of thiolglyoxalines, glyoxalines, and thiocarbamides and is not specific for the thiol group. Thiocarbamides give nothing distinctive and in the glyoxaline group the reaction is probably of value for the diagnosis of constitution. Whilst 2-thiol-4(or 5)-methylglyoxaline gives an eosin-red solution which on careful addition of acid becomes blue, other glyoxalines, when they do give a colour, generally give a yellow or orange-yellow solution which may or may not be discharged by acids. In some cases, the yellow colouring matter is soluble in chloroform. Thus 4(or 5)-methylglyoxaline gives a bright yellow solution, 2-thiol-1 : 4-dimethylglyoxaline gives a yellow solution, whilst its isomeride, 2-thiol-1 : 5-dimethylglyoxaline, gives no colour. Again, 2-thiol-1-phenylglyoxaline gives no colour, whereas 2-thiol-1-phenyl-4-methylglyoxaline gives a bright yellow colour in the aqueous and chloroform layers. The reaction seems to be conditioned by the presence of at least one substituent in the 4- or 5-position, but both may be substituted if carboxyl or carbethoxyl is one, as these probably suffer replacement. Finally, if the hydrogen attached to nitrogen is displaced, only the 1 : 4-disubstituted derivatives produce colour. The reaction is possibly dependent on the formation of the triglyoxaline analogues of the triphenylmethane dyes.

A reaction which appears to be new for thiocarbamides and 2-thiolglyoxalines is the intense blue colour produced when an ammoniacal solution of the substance to be tested is treated with a drop of phosphomolybdic acid. This reagent shows the great ease with which 4(or 5)-carbethoxy-5(or 4)-methyl-2-glyoxaline disulphide is hydrolysed with production of the thiol group by very brief boiling in ammoniacal solution.

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CCXLI.—*Chemical Action at an Interface: The Production of Acidity in Neutral Salt Solutions.*

By N. Venkatanarasimha Achar and Francis L. Usher.

The frequently noticed development of acidity in neutral salt solutions in the presence of material from which no detectable quantity of acid can be extracted by pure water can be accounted for by assuming (1) a simple chemical interaction between the salt and a definite acid or mixture of acids, (2) a preferential absorption of the base of the salt, or (3) an exchange between the kations of the salt and hydrogen ions previously adsorbed by the material (Mukherjee, *J. Indian Chem. Soc.*, 1925, **2**, 191). The second explanation assumes the selective adsorption of hydroxyl ions from water, and can evidently be employed, alternatively with the third, to account for acidity produced by materials which are not regarded as actual or potential acids.

The first, or "chemical," theory has been objected to on the ground that, if the materials dealt with contain acids, the latter must be both insoluble, since the water extracts are neutral, and strong, in that they are able to decompose salts of the strong mineral acids; but no acids of this character are known. The purpose of this paper is to show that the effects observed with materials of complex and undetermined composition may also be observed with a simple insoluble weak acid; that these effects may properly be regarded as arising from an ordinary chemical interaction of the ionic type, qualified by the circumstance that one of the ions is non-diffusible; and that their occurrence is a logical consequence of the "surface dissociation" theory. This theory was developed by Pauli in connexion with colloidal suspensions, and advocated by McBain in the case of electrokinetic phenomena, and it does not require the assumption of selective adsorption.

If the molecules in the surface of an insoluble acid in contact with water are imagined to undergo dissociation, and if the hydrogen ions so produced are osmotically active and have a range of movement determined by the electrostatic field due to the residual acid anions on the surface, such a system is separated from the external liquid by an imaginary envelope which marks the extreme range of movement of the hydrogen ions, and is equivalent to a membrane permeable by any ions except the acid anions embedded in the surface of the insoluble acid. When the external liquid is pure water, this, on separation from the insoluble acid, should not have acquired hydrogen ions from the latter, since they are electrostatically tethered to its surface; but if a neutral salt is present in the water,

an exchange should take place between some of the hydrogen ions within the envelope and an electrically equivalent number of kations in the external liquid. On the foregoing assumptions, a solution of a neutral salt in contact with, *e.g.*, stearic acid, should become acid, and the total acid present should increase with increase of the volume of solution per unit surface of the solid, in consequence of the progressive dissociation of the molecules in the surface; or alternatively, if this ratio is kept constant, the acidity should vary directly with the concentration of the salt within the limits denoted by the principle of "membrane equilibrium." The experiments with stearic acid described below confirm these expectations, and suggest an equally simple explanation of the results obtained by Mukherjee and his co-workers (J., 1926, 3023) in the case of hydrated silica.

EXPERIMENTAL.

Some experiments were carried out with colloidal suspensions of stearic acid in water, in order to ascertain the order of magnitude of the acidity, if any, produced in neutral solutions of potassium chloride. The stearic acid used (Kahlbaum's best) was recrystallised twice from neutral methyl alcohol. It was shown that this degree of purification furnished a material the solubility of which in water ($3{\cdot}5 \times 10^{-6}$ equiv. per litre) was not further reduced by repeated recrystallisation (compare Bowden, J., 1911, **99**, 192; Bunbury and Martin, J., 1914, **105**, 418). The acid was dispersed by dropping a dilute methyl-alcoholic solution into boiling "conductivity" water contained in a large Jena-glass flask, the methyl alcohol being removed by continued boiling. To 50 c.c. of this suspension 25 c.c. of a neutral solution of potassium chloride were added, and the mixture was either filtered through an "ashless" filter, or, if coagulation was incomplete, submitted to ultrafiltration through a collodion membrane, the first portions of the filtrate being rejected. 10 C.c. of the clear liquid were then titrated against standard sodium hydroxide, and the acidity was calculated after the value obtained by titrating the ultrafiltrate from a suspension in water alone had been subtracted. The last-named ultrafiltrate was considered to be a saturated solution of stearic acid in water, but the solubility as determined from it is probably slightly in excess of the true value, because the liquid, in spite of its apparent clarity, may have contained a few ultramicronic and amicronic particles. The true values of the acidity due to the salt action should probably therefore be rather higher than those in Table I. It is also to be observed that, although atmospheric carbon dioxide was not rigidly excluded, the solubility determination itself constituted a control

experiment, so that any error due to this cause can only be a difference between two small and nearly equal errors.

The liquids, excepting the alkali contained in the microburette, were handled in vessels coated with hard, neutral paraffin wax, and the experiments were carried out at the ordinary temperature (about 23°). The results are in Table I.

TABLE I.

50 c.c. Stearic acid suspension + 25 c.c. KCl solution.

Normality of KCl in mixture ...	0·001	0·007	0·027	0·083	0·33	0·84
Normality ($\times 10^6$) of acid due to salt action	6	7	16	26	32	49

A second series of experiments had for its object the accurate determination at the ordinary temperature of the relation between acidity and salt concentration, and between acidity and the volume of salt solution per unit surface of stearic acid. The method used was the electrical measurement of the hydrogen-ion activity of mixtures of stearic acid suspensions with neutral solutions of potassium sulphate. The hydrogen-ion activity of solutions of potassium sulphate at the three dilutions employed, when containing various known quantities of sulphuric acid, was also measured separately, and curves were drawn from which the actual quantity of sulphuric acid liberated by the suspensions could be read off. Preliminary experiments with an ordinary hydrogen electrode were discontinued on account of the unsatisfactory readings obtained, due possibly to the spoiling of the platinised surface of the electrode by particles of stearic acid. A bright platinum quinhydrone electrode gave satisfactory and reproducible results.

The quinhydrone, stearic acid, and potassium sulphate were recrystallised several times, the best-quality "conductivity" water was used, and no liquid of which the hydrogen-ion activity was to be measured was ever in contact with glass other than well-steamed Jena-glass or glass coated with neutral, hard paraffin wax. The liquid was deprived of dissolved carbon dioxide, before measurements were made, by prolonged passage of carbon dioxide-free air saturated with the vapour of the liquid under examination. A "saturated" calomel electrode was used as the second pole of the combination the *E.M.F.* of which was measured, and the combination was kept on an earthed metal sheet in a large air thermostat at 29° (the room temperature during these experiments being usually 27—28°). In order to avoid contact of the liquids with soda-glass measuring vessels, the solutions were prepared in every case by weight, not volume. The solutions of known acidity were made up by adding sulphuric acid of known strength contained in a paraffined

weight-pipette to 25 g. of potassium sulphate solution of double the strength required, in a tared Jena-glass flask, the final weight being then made up to 50 g. with conductivity water. The stearic acid mixtures contained equal weights of the suspension and of the potassium sulphate solution. If coagulation occurred before dissolved carbon dioxide was removed, as it did with the $N/2$-salt solutions at all dilutions except the highest, the liquid was filtered through an " ashless " paper, and the first 10 c.c. were rejected. If coagulation occurred either not at all or only after the bubbling of air, the unfiltered liquid was used. The relative hydrogen-ion activities were calculated from the formula $\log f = (E - 0{\cdot}4536)/0{\cdot}0598$, in which E denotes the measured $E.M.F.$ of the combination. The values of the hydrogen-ion activities corresponding to various concentrations of sulphuric acid in the three solutions of potassium sulphate used are in Table II. The figures are calculated on the assumption that the potential at the K_2SO_4–saturated KCl junction is zero, an assumption which does not affect their validity for the purposes of this investigation.

TABLE II.

	$N/100$-K_2SO_4.						
Conc. of H_2SO_4 ($N \times 10^6$) ...	26·80	6·77	4·97	2·02			
Relative $H^{\cdot}$ activity ($\times 10^6$)	15·45	4·45	3·57	1·62			
	$N/10$-K_2SO_4.						
Conc. of H_2SO_4 ($N \times 10^6$) ...	55·8	28·0	20·07	14·55	6·89	4·64	2·72
Relative $H^{\cdot}$ activity ($\times 10^6$)	17·42	8·38	6·72	4·58	2·47	1·73	1·19
	$N/2$-K_2SO_4.						
Conc. of H_2SO_4 ($N \times 10^6$) ...	269	145	52·8	33·66	20·79	13·06	5·94
Relative $H^{\cdot}$ activity ($\times 10^6$)	39·84	21·52	6·78	3·88	2·26	1·57	1·10

Table III gives the results of the measurements of acidity produced by the stearic acid suspensions. The figures headed " dilution " refer to dilutions of the stock suspension which contained 2·32 g. of stearic acid per litre. Columns A, B, and C contain, respectively, the relative hydrogen-ion activities ($\times 10^6$), the concentration of acid (g.-equivs. $\times 10^6$ per kg.), and the total acid liberated (g.-equivs. $\times 10^6$ per g. of stearic acid). The figures are calculated from the mean of two or more separate measurements in each case.

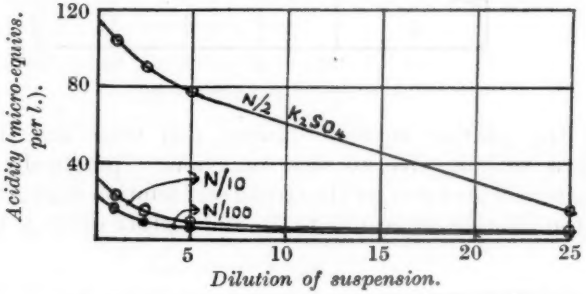
TABLE III.

	Normality of K_2SO_4 solution.								
	$N/100$.			$N/10$.			$N/2$.		
Dilution.	A.	B.	C.	A.	B.	C.	A.	B.	C.
1	10·4	16·2	13·9	7·75	23·3	20·1	15·4	105	90·6
2·5	6·52	8·8	18·9	5·14	14·8	31·9	12·8	91·5	197
5	4·98	6·0	25·8	3·35	8·5	36·6	10·6	77·6	333
25	3·88	4·14	89·6	2·12	4·4	94·8	1·98	15·8	340

The Nature of the Reaction between an Insoluble Acid and Salt Solutions.

The application of the theory of " membrane equilibrium " to the present problem is complicated by two factors which were not included in the theory as originally formulated by Donnan, *viz.*, (1) the unknown ratio of the volumes of liquid on either side of the " membrane," and (2) incomplete dissociation of the non-diffusible substance, involving the possibility of an increase in the number of diffusible ions available for exchange. In the absence of any knowledge of the magnitude of these factors, no quantitative application of the theory is possible; but an examination of the results of the experiments just described is strongly in favour of the conclusion that the reaction under discussion (and, by implication, similar reactions in which acidity is produced in neutral salt solutions) is qualitatively accounted for by the theory.

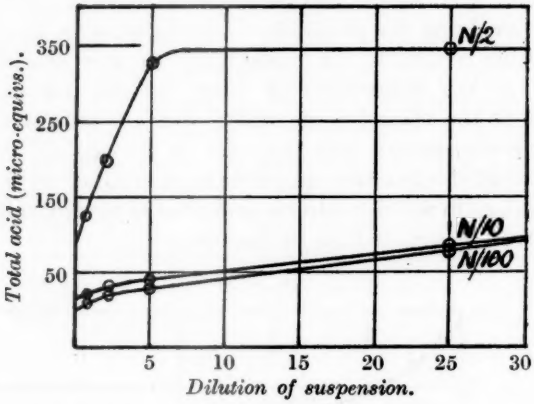
FIG. 1.



The progressive dilution of a suspension by the salt solution used is equivalent to increasing the volume of the liquid containing only diffusible ions, while maintaining constant that of the liquid containing the non-diffusible ion. If no dissociation of the surface molecules of the insoluble acid takes place, the activity of the hydrogen ions in the external liquid should decrease in an approximately linear manner with the dilution, provided that the volume of the external liquid is always a large fraction of the total volume, as it almost certainly is when the suspension is dilute. Assuming, on the other hand, that the surface molecules are initially but slightly dissociated, then if there were an unlimited supply of such molecules, which could undergo progressive dissociation, the hydrogen-ion activity in the external liquid should show little change with dilution. Under the experimental conditions the supply of surface molecules is limited, and it can be seen from Fig. 1 that, at the higher dilutions, the observations nearly correspond to these two extreme cases. Since a concentrated salt solution produces a more complete

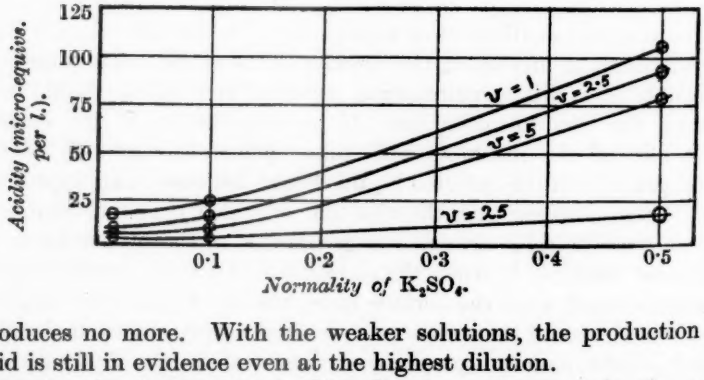
exchange of ions than do the more dilute solutions, the reserve of undissociated molecules is in the former case nearly exhausted initially, and very little further dissociation is possible as the volume is increased; on the other hand, in the dilute solutions the acid concentration is comparatively little affected by dilution. Fig. 2,

FIG. 2.



showing the relation between dilution and total acid liberated, provides a striking clue to this behaviour: practically all the available acid is liberated by the strong salt solution during the early part of the dilution process (1 to 5), and further dilution (5 to 25)

FIG. 3.



produces no more. With the weaker solutions, the production of acid is still in evidence even at the highest dilution.

Again, the increase of acidity due to an increase in the concentration of potassium sulphate (see Fig. 3) is, at least qualitatively, predicted by the theory of membrane equilibrium. The increase is considerably greater than would be expected in a system where the number of exchangeable ions is constant, and this constitutes

additional evidence of the dissociation of the surface molecules under the experimental conditions.

The Relation between Acid Concentration and Hydrogen-ion Activity.

Donnan's theory is concerned with activities rather than concentrations, but in the present experiments the activity relationships tend to be obscured by disturbing factors incidental to the method used. In the presence of an excess of potassium sulphate, any sulphuric acid liberated is present as potassium hydrogen sulphate which, itself a strong binary electrolyte, furnishes an anion which is an acid with a dissociation constant of about 10^{-2} (Drucker, *Z. physikal. Chem.*, 1920, **96**, 382). An increase in the concentration of potassium sulphate may therefore be expected to influence the hydrogen-ion activity and the acid concentration in opposite senses, because a higher concentration of the salt, whilst effecting a more complete exchange of hydrogen ions, will at the same time cause a greater proportion of them to assume an inactive condition. This is, in fact, observed, for the activity–salt concentration curves pass through a minimum except at the highest dilution of the suspension.

Although it is chiefly a matter of terminology whether the production of acid, in circumstances similar to those considered in this paper, is to be regarded as an ionic exchange or as a chemical reaction between equivalent quantities of two molecular species, the suggestion has been put forward (Mukherjee, *loc. cit.*), in the case of hydrated silica, that the production of acid is to be attributed to an exchange of *adsorbed* ions bearing no stoicheiometric relation to the number of molecules of silica associated with them. The point of view advocated here differs radically from Mukherjee's in regarding the action as taking place between quantities of the insoluble acid and the neutral salt which are in a simple stoicheiometric proportion; in other words, one is dealing with a reversible chemical change differing from the ordinary type only in its localisation at an interface. The advantages of this point of view are that it does not need to invoke any of the various types of adsorption, and is at once in harmony with accepted chemical theory and with a theory of interfacial behaviour for which there is a rapidly increasing body of evidence (see *Trans. Faraday Soc.*, 1925, **21**, 406).

Summary.

1. The production of acidity by suspensions of stearic acid has been measured in neutral solutions of potassium chloride and potassium sulphate.

2. The variation of hydrogen-ion activity and of total acid with the salt concentration and with dilution of the suspension has been

examined, and found to be consistent with the view that the observed acidity is produced by exchange of the kations of the salt with hydrogen ions formed from dissociating molecules in the surface of the insoluble acid.

3. It is considered that the production of acidity in neutral solutions of salts of strong acids in contact with an extensive surface of a weak insoluble acid is generally to be expected on the basis of accepted theory, and is capable of a simple chemical interpretation.

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CCXLII.—*Reactions of Incandescent Tungsten with Nitrogen and with Water Vapour.*

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(COMMUNICATION FROM THE RESEARCH STAFF OF THE GENERAL ELECTRIC COMPANY, LTD., WEMBLEY.)

1. *Reaction with Nitrogen.*

THE temperature at which a tungsten filament can be operated in a vacuum is in practice limited by the rate of evaporation of the metal, which forms a black deposit on the bulb, thereby reducing the candle power of the lamp. By surrounding the filament with an atmosphere of inert gas, the loss of metal by evaporation is reduced, and the filament can be operated at a higher temperature, and therefore at a higher efficiency, for an equal life (Brit. Pat., 10,918, 1913). In lamps of small wattage, it is customary to use as the inert gas a mixture of argon and nitrogen containing 10—20% of the latter, but lamps of 500 watts and upwards are frequently filled with pure nitrogen on grounds of economy. The filaments operate at a temperature of about 2850° K. It is found that a dark brown deposit is slowly formed on the inside of the bulb during the life of such lamps; but it forms much more slowly if an argon–nitrogen mixture is used. The cause of this coloration has now been investigated.

Very little information exists as to the formation, composition, or properties of the nitrides of tungsten. Henderson and Galletly (*J. Soc. Chem. Ind.*, 1908, **27**, 387) heated tungsten powder to 860° in a current of ammonia, but the product contained only a trace of nitrogen. By heating "tungsten nitramide," $W_3N_6H_4$, in ammonia, Uhrlaub ("Die Verbindungen einiger Metalle mit Stickstoff," Göttingen, 1859) obtained a substance to which he

assigned the formula W_3N_2. By heating tungsten hexachloride in ammonia, Rideal (J., 1889, **55**, 41) obtained a black, metallic-looking powder, the composition of which was represented as W_2N_3.

Langmuir (*J. Amer. Chem. Soc.*, 1913, **35**, 931) has studied the rate at which nitrogen is absorbed in a tungsten-filament vacuum lamp. He found that this was dependent on the rate of evaporation of the filament, and that one molecule of nitrogen disappeared for each atom of tungsten evaporated. He therefore assumed that nitrogen did not react with solid tungsten at temperatures in the neighbourhood of 2200° K., but that when an atom of tungsten struck a molecule of nitrogen they combined to form WN_2, which was deposited on the bulb. This nitride is described as a brown compound, readily decomposed by water to form ammonia and tungstic oxide, WO_3. No direct analyses were made.

It appeared probable that the coloration of the lamps under consideration might be due to the formation of such a nitride. Alternatively, it was possible that the deposit was evaporated tungsten from the filament, or nickel or molybdenum from the supporting and leading-in wires. The presence of traces of oxidising gases might also give rise to oxides of any of these metals. The total weight of the deposit on the inside of the largest lamps, which have a capacity of about 4 litres, is only 5—10 mg. after the lamp has been operated for 1000 hours. Special methods of analysis had, therefore, to be developed.

Preliminary Examination.—On opening the lamp a distinct odour is observed, which resembles ammonia, but is difficult to identify. The deposit can easily be rubbed off with the finger, or scraped together with a knife. After being exposed to the air for an hour, it becomes slightly sticky, more difficult to remove, and somewhat lighter in colour. After two or three days' exposure, it is again quite dry and easily rubbed off. A small quantity was ignited in air and gave a greenish-yellow residue, which resembled tungstic oxide and yielded its characteristic *X*-ray pattern, thus proving that the original material was definitely tungsten or one of its compounds.

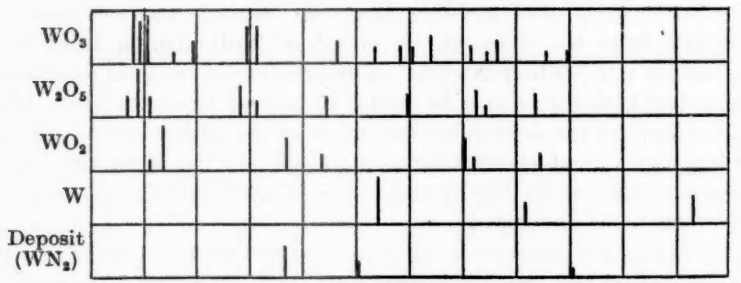
X-Ray Examination.—Tungsten forms three oxides, which are readily distinguished by their colour: WO_3, yellow; W_2O_5, deep blue; and WO_2, chocolate-brown. Pure specimens of each of these oxides were prepared, and the characteristic *X*-ray diffraction patterns obtained, together with that of the metal. These are shown in Fig. 1, where the height of the lines represents their relative intensities on the film. A little of the deposit was then smeared on a piece of tissue paper, and exposed to the *X*-ray beam. Three strongly marked but somewhat diffuse lines appeared in the

pattern. Although they were sufficiently clear for purposes of identification, it was not easy to measure their position accurately. The diffuseness was due to the extremely fine state of division of the deposit. By heating another sample at 600° in a current of pure, dry argon for 2 hours, the particles became coarser, and the lines in the diffraction pattern appeared much sharper. Their position, however, was unchanged. This pattern is also shown in Fig. 1. On comparing the positions of the lines with those in the patterns of the metal and its oxides, it is clear there is no correspondence and that the deposit must be some other compound.

Spectroscopic Examination.—The fact that the material burnt readily in air to tungstic oxide suggested a simple way of proving whether it was a nitride, for nitrogen should be formed when such a compound is oxidised.

FIG. 1.

X-Ray diffraction patterns of tungsten compounds.

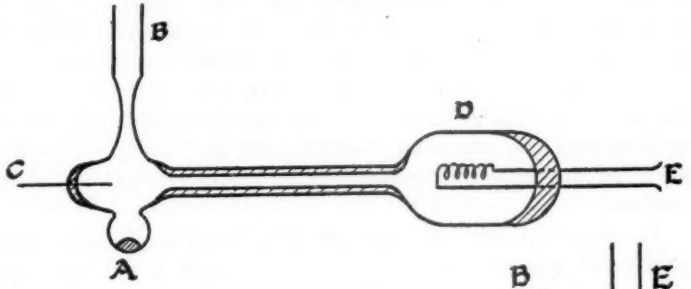


A small hard-glass spectrum tube was made as shown in Fig. 2. This had a bulb, A, into which a mixture of the deposit with a little potassium permanganate was introduced through B. A plain molybdenum electrode, C, was arranged at this end, whilst at the other end of the tube a thick tungsten spiral filament, D, acted as the second electrode for the discharge. The electrodes were thoroughly freed from gas before the mixture was introduced, after which the tube was evacuated and sealed off. The whole volume of the apparatus was less than 1 c.c., and since a pressure of about 1 cm. was sufficient to obtain a satisfactory discharge, only 0·0003 g. of material was necessary.

On heating the bulb, A, a vigorous reaction occurred between the material and the permanganate. On passing a discharge, the spectrum of both nitrogen and oxygen appeared. The excess oxygen, derived from the permanganate, was then removed by heating the tungsten filament, and finally the tube contained nearly

pure nitrogen. The material was therefore most probably a nitride of tungsten having the formula WN_x.

FIG. 2.
Discharge tube.



Composition of the Nitride.—The value of x was determined by measuring (*a*) the volume of oxygen required to burn a small weight of the material, and (*b*) the volume of nitrogen evolved. From the equation

$$2WN_x + 3O_2 = 2WO_3 + xN_2,$$

it is seen that the value of x is determined from the ratio of the volumes of oxygen and nitrogen. It is not necessary to know the weight of the nitride, but, as a further check on the analysis, the material was weighed before the combustion was carried out. A special form of combustion apparatus was made (Fig. 3) which consisted of a hard-glass tube, A (volume about 3 c.c.), attached to a tap, B, and to a piece of barometer tubing, C (volume 1·5 c.c.). The lower end of the barometer tube was connected by a flexible rubber tube to a second piece of barometer tubing, D. The volume of the apparatus was carefully calibrated and a scale was attached to the tube C.

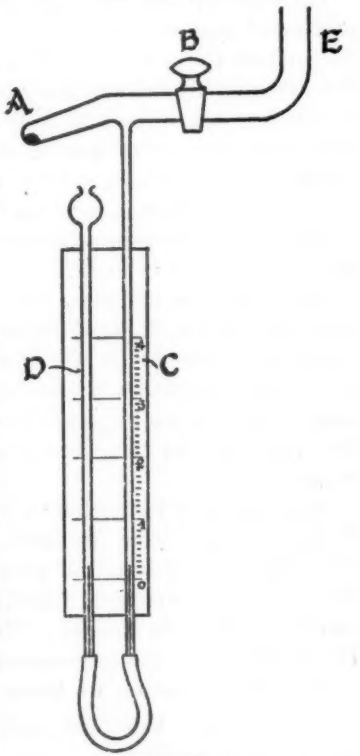


FIG. 3.
Combustion apparatus.

A weighed quantity (2—3 mg.) of the nitride was introduced into the limb A. The barometer U was filled with mercury up to about

the scale zero, and the tap closed. The whole apparatus was carefully protected from draughts and allowed to attain a steady temperature, which was read on an attached thermometer. The pressure was adjusted and the scale reading gave the volume of air in the apparatus. The nitride was then heated to about 650° by means of a blow pipe; it burnt readily to the yellow oxide, WO_3, and nitrogen was liberated. The apparatus was allowed to cool to room temperature during 5—10 hours, the pressure was adjusted, and the new volume read off. The difference between this reading and the previous one, after correction for any change of temperature, gave the volume of oxygen absorbed minus the volume of nitrogen evolved.

The external limb, E, was now filled with an alkaline solution of pyrogallol and the apparatus tilted so that when the liquid was drawn into the wide limb it would not enter the barometer tube. By lowering or raising the tube D, the solution was alternately drawn into the apparatus and expelled. The walls of the tube A were thus repeatedly wetted with fresh liquid until the remaining oxygen was absorbed. After allowing the apparatus to attain a steady temperature, a new reading of the volume was taken. This represented the known volume of nitrogen originally in the apparatus plus the nitrogen evolved.

The apparatus had been originally filled with atmospheric air, the humidity of which was determined from wet and dry bulb thermometer readings. It was found that the water-vapour pressure was, within the limits of accuracy attainable in the experiments, the same as that of the 40% caustic soda solution used for the absorption. No correction for the vapour pressure of the liquid was therefore required.

Although the formation of oxides of nitrogen during the combustion did not seem probable, caustic potash was introduced into the apparatus before the pyrogallol solution in one experiment. No absorption occurred, thus indicating that no oxides higher than nitrous oxide were present. It was thought justifiable to neglect the possibility of the presence of the latter.

From the equation we have

$$x/3 = \text{Vol. of } N_2 \text{ evolved/Vol. of } O_2 \text{ absorbed.}$$

Let c be the volume of nitrogen evolved and b the contraction on burning. Then

$$b = \text{Vol. of oxygen} - c,$$

and

$$x = 3c/(b + c).$$

After a number of preliminary trials to test the apparatus, two accurate determinations were made with weighed quantities of

materials from two different lamps. The results are given in Table I.

TABLE I.

Expt.	Weight of material (g.).	*b* (c.c.).	*c* (c.c.).	*x*.
1	0·0026	0·10	0·19	1·96
2	0·0036	0·15	0·27	1·93

These values show very good agreement and indicate that the nitride has the formula WN_2. Assuming this to be correct, it is possible to check the values obtained for *c* from the weight of material used. In both cases, the experimental value is about 70% of the theoretical value for the volume of the combined nitrogen. The difference is probably accounted for by the presence in the material of small fragments of glass and mica, with which it becomes unavoidably contaminated when the lamp is broken open.

These results confirm the conclusion reached by Langmuir as to the composition of the nitride, by an entirely different method. The formulæ assigned by earlier workers are probably in error owing to the difficulty of separating the nitride from the metal powder, and to the inherent difficulties of gravimetric methods when dealing with oxides and nitrides of tungsten, the molecular weights of which are so nearly the same.

The approximate density of the nitride was determined by weighing samples of 5—10 mg. in air and in benzene. A small pellet of the material was pressed in a steel die, and weighed in a pan made from aluminium foil which weighed only 8 mg. The pan holding the pellet was immersed in benzene in an evacuated vessel, in order to remove any occluded air, and its weight in the liquid then determined. The method was checked by determining the density of a pellet made from a thin film of tungstic oxide condensed on a glass surface; this gave a value of 6·3 g. per c.c., the density of fused crystalline tungstic oxide being 7·2 g. per c.c. Two determinations of the density of the nitride gave a mean value of 5 g. per c.c., with a maximum error of $\pm 0{\cdot}5$ unit.

2. *Reaction with Water Vapour.*

The action of water vapour on an incandescent tungsten filament has been described previously by one of us (Smithells, *Trans. Faraday Soc.*, 1921, **17**, 485). It was shown that a reversible reaction took place in which tungsten was oxidised at the hotter parts of the filament, and the oxide reduced to metal at lower temperatures and deposited on the cooler parts of the filament: $W + 2H_2O \rightleftharpoons WO_2 + 2H_2$. The reaction is accompanied by a

gradual blackening of the bulb, and it would be expected that this is due to a certain amount of both metal and oxide being carried by convection in the gas. Langmuir (*Gen. Electric Rev.*, 1926, **29**, 153) has shown, however, that atomic hydrogen, which is formed when molecular hydrogen comes in contact with incandescent tungsten, will reduce tungsten oxides at room temperature. It therefore appeared of interest to determine the nature of the deposit, which is nearly black and easily distinguishable from the nitride just described. The *X*-ray diffraction pattern was found to be identical with that obtained from pure tungsten powder, no trace of oxide being present. This can only be explained by assuming that atomic hydrogen formed during the reaction, and in contact with the incandescent filament, arrives at the surface of the glass and reduces any oxide deposited. That oxide molecules do reach the glass walls is almost certain, since the cyclic action can hardly be so complete as to prevent their escape entirely. The fact that they are subsequently reduced explains why even very minute quantities of water vapour have such a deleterious effect in gas-filled lamps. Water vapour present in the filling gas to the extent of 1 part in 10,000 parts will cause the filament to burn out in less than an hour.

GENERAL ELECTRIC COMPANY, LTD.,
WEMBLEY.

[*Received, February 22nd*, 1927.]

CCXLIII.—*The Intermolecular Condensation of Styryl Methyl Ketones. Part I.*

By ROBERT DICKINSON, ISIDOR MORRIS HEILBRON, and FRANCIS IRVING.

IN a previous investigation (Dickinson and Heilbron, this vol., p. 14), 3 : 4-dimethoxystyryl methyl ketone was required. Apparently three different substances, m. p.'s 168° (Francesconi and Cusmano, *Gazzetta*, 1908, **38**, ii, 70), 85—86°, and 91—92° (Ryan and Plunkett, *Proc. Roy. Irish Acad.*, 1916, **32**, *B*, 199; Kaufmann and Radosević, *Ber.*, 1916, **49**, 675), are recorded in the literature under this name, all having been prepared by the alkali condensation of veratraldehyde with acetone.

We have now investigated these compounds in detail. The second and the third are undoubtedly identical, the true melting point being 86°. This compound is definitely 3 : 4-dimethoxystyryl methyl ketone, for (1) its molecular weight, determined

ebullioscopically, is normal; (2) in the presence of hydrogen chloride, it condenses with 2-naphthol-1-aldehyde, giving 3-3′ : 4′-dimethoxystyryl-β-naphthapyrylium chloride (Dickinson and Heilbron, *loc. cit.*); (3) it may be prepared by the methylation of 3-methoxy-4-hydroxystyryl methyl ketone; (4) it absorbs one molecule of bromine (the dibromide, however, could not be isolated); and (5) it readily condenses with veratraldehyde, in the presence of alkali, giving 3 : 3′ : 4 : 4′-tetramethoxydistyryl ketone, identical with the product obtained by Stobbe and Haertel (*Annalen*, 1909, **370**, 104), the constitution of which we have now confirmed by the preparation of its tetrabromide. Guimbal (*Dipl. et Sup.*, No. 212, Paris, 1921; compare Faillebin, *Ann. Chim.*, 1925, **4**, 445) has come to the same conclusion, but only on the results of analysis and cryoscopy; he records 84° as the melting point. Lapworth and Wykes (J., 1917, **111**, 790) also must certainly have had this same ketone in their hands, as was shown by the ease with which it was oxidised to dimethylcaffeic acid. They do not, however, give the method of preparation, or record the melting point of their product, but only refer to Francesconi and Cusmano (*loc. cit.*), whose product is entirely different and cannot yield dimethylcaffeic acid.

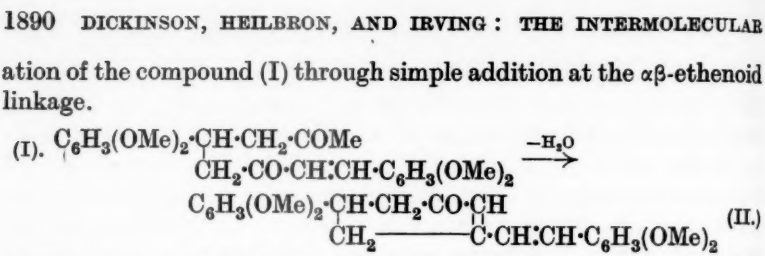
The compound described by Francesconi and Cusmano (*loc. cit.*) has also been obtained by other workers, who, beyond stating that it is not veratrylideneacetone and making suggestions as to its possible constitution, have not investigated it experimentally. It is regarded by Ryan and Plunkett (*loc. cit.*) as an isomeric form of the styryl ketone, by Kaufmann and Radosević (*loc. cit.*) as the corresponding distyryl ketone, and by Guimbal (*loc. cit.*) as a compound of 3 : 4-dimethoxystyryl methyl ketone and acetone. Francesconi and Cusmano (*loc. cit.*) do not record any analytical values for their compound, or for its alleged condensation product with cinnamaldehyde.

We have now found that in addition to its direct preparation from veratraldehyde and acetone, the 168°-compound may be obtained by treating 3 : 4-dimethoxystyryl methyl ketone with alkali, acetone being used as solvent in order to minimise the production of the distyryl ketone through scission (compare Heilbron and Buck, J., 1921, **119**, 1503). Our analyses show that the substance is formed according to the equations:

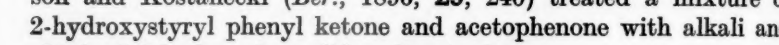
(A) $2C_6H_3(OMe)_2\cdot CHO + 2Me_2CO = C_{24}H_{26}O_5 + 3H_2O$
(B) $2C_6H_3(OMe)_2\cdot CH{:}CH\cdot CO\cdot CH_3 = C_{24}H_{26}O_5 + H_2O$.

From a knowledge of the addition reactions of unsaturated ketones, the first stage in equation (B) is undoubtedly represented by form-

ation of the compound (I) through simple addition at the αβ-ethenoid linkage.

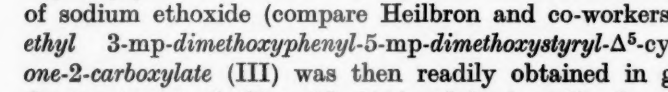


Many examples of such addition reactions are known; *e.g.*, Cornelson and Kostanecki (*Ber.*, 1896, **29**, 240) treated a mixture of 2-hydroxystyryl phenyl ketone and acetophenone with alkali and obtained 2-hydroxybenzylidenediacetophenone:



Styryl and distyryl ketones add on acetoacetic ester and other keto-esters in precisely the same way, although secondary reactions occur afterwards (compare Heilbron and co-workers, J., 1924, **125**, 340, 2064; 1925, **127**, 2159; this vol., p. 918). The second stage of reaction (B) consists in the elimination of a molecule of water from compound (I), and this would almost certainly occur in such a manner as to yield the *cyclo*hexenone derivative (II).

The reactions of the 168°-compound are in full agreement with this formulation. We have determined its molecular weight, which is normal, and prepared its semicarbazone. It readily absorbs two molecules of bromine with exhibition of halochromy, but we have been unable to isolate the tetrabromide in a state of purity. Finally, full confirmation of formula (II) has been reached by the synthesis of the compound in the following way. 3 : 3′ : 4 : 4′-Tetramethoxydistyryl ketone was condensed with acetoacetic ester by means of sodium ethoxide (compare Heilbron and co-workers, *loc. cit.*); *ethyl* 3-mp-*dimethoxyphenyl*-5-mp-*dimethoxystyryl*-Δ^5-cyclo*hexen*-1-*one*-2-*carboxylate* (III) was then readily obtained in good yield. On treatment of this with 20% sulphuric acid, the carbethoxyl was eliminated with production of the free *cyclo*hexenone (II), which was identical in all respects with the compound described by Francesconi and Cusmano.



We have attempted to obtain by similar means compounds analogous to (II), and for this purpose we prepared the *ethyl*, n-*propyl*, iso*propyl*, and *benzyl* ethers of 3-methoxy-4-hydroxystyryl methyl ketone. On treating these with alkali, we obtained the homologue of (II) in only one case—the *n*-propyl compound—and its reactions are in harmony with such a structure. An abnormal result was obtained with 3-*methoxy*-4-*benzyloxystyryl methyl ketone*,

treatment with alkali yielding a new substance (m. p. 174—175°) which gave analytical results for 3 : 3′-dimethoxy-4 : 4′-dibenzyloxydistyryl ketone, but was different from the distyryl ketone prepared in the usual manner (m. p. 155°). In all cases, much resinous material was formed; apparently the inter-condensation of styryl methyl ketones does not stop at the stage represented by equation (B), but continues to give a mixture of still more complex products. Such resinification of unsaturated ketones has already been considered by Borsche (*Ber.*, 1909, **42**, 4499), Giua (*Gazzetta*, 1925, **55**, 567), and especially by Herzog (*Z. angew. Chem.*, 1922, **35**, 465, 641; 1923, **36**, 471; *Chem.-Ztg.*, 1925, **49**, 119).

We next directed our attention to the action of piperidine upon styryl methyl ketones, expecting that this base would behave similarly to alkali, but would be milder in its action and possibly yield the primary additive compound (I). In all the cases we have investigated, however, much resinification took place, and we have been able to isolate solid products only in minute yields. These compounds are not true intermolecular condensation products, but dimerides of the styryl ketone, and from their saturated nature and absence of colour they must be regarded as *cyclo*butane derivatives (IV or V) analogous to that obtained by Stobbe (*J. pr. Chem.*, 1912, **86**, 248; Stobbe and Hensel, *Ber.*, 1926, **59**, 2254)

(IV.) $\begin{matrix} \text{R·CH·CH·COMe} \\ \text{R·CH·CH·COMe} \end{matrix}$ $\qquad$ $\begin{matrix} \text{R·CH·CH·COMe} \\ \text{COMe·CH·CHR} \end{matrix}$ (V.) $\qquad [\text{R} = \text{C}_6\text{H}_3(\text{OMe})_2]$

from phenyl 4-methoxystyryl ketone by the same method, and also to the compounds he and other workers have obtained by photopolymerisation (compare Stobbe and Hensel, *loc. cit.*).

Wieland (*Ber.*, 1904, **37**, 1145) obtained a dimeric form of phenyl styryl ketone by treating it with acetic anhydride containing a trace of sulphuric acid; but, applied to our compounds, this method yielded resinous material only, from which no pure substance has been isolated.

Experimental.

3 : 4-Dimethoxystyryl methyl ketone was prepared by Kaufmann and Radosević's method (*loc. cit.*) and found to melt at 85—86°, as given by Ryan and Plunkett (*loc. cit.*). The ketone can also be obtained in quantitative yield by the methylation of 3-methoxy-4-hydroxystyryl methyl ketone by Dickinson's method (J., 1926, 2234) for the preparation of 2-methoxystyryl benzyl ketone (Found: *M*,* 234, 207, 203. $C_{12}H_{14}O_3$ requires *M*, 206).

* The molecular weights recorded in this paper were all determined ebullioscopically in chloroform by Menzies's method (Menzies and Wright, *J. Amer. Chem. Soc.*, 1921, **43**, 2314).

The *semicarbazone*, prepared by the usual method, crystallises from alcohol in colourless needles, m. p. 205°, which exhibit phototropic properties, becoming sulphur-yellow on short exposure to light. Crystallised from 50% acetic acid, it forms canary-yellow needles melting indefinitely about 180°. This is probably an unstable acetate, for on treatment with water or on keeping over potash it loses its crystalline form and colour, becoming identical with the original semicarbazone (Found: N, 16·1. $C_{13}H_{17}O_3N_3$ requires N, 16·0%).

3 : 3′ : 4 : 4′-Tetramethoxydistyryl ketone was obtained in fair yield by the direct alkaline condensation of veratraldehyde with acetone according to Stobbe and Haertel's method (*loc. cit.*). It was also readily prepared by condensation of 3 : 4-dimethoxystyryl methyl ketone (1·3 g.) with veratraldehyde (1 g.) in alcoholic solution (20 c.c.) in presence of dilute aqueous sodium hydroxide (3 c.c. of 8%); after a few hours, the yellow precipitate was collected and crystallised from alcohol, yielding the pure product, m. p. 84°. A peculiar property of this distyryl ketone was noted: a specimen which had been kept in a sealed tube for several months changed in colour, the golden-yellow crystals becoming yellowish-brown, and crumbled to a powder. The change appeared to start at various centres and slowly spread into the surrounding material, but complete conversion was never attained. The *tetrabromide*, prepared by treating the ketone in chloroform solution with the calculated amount of bromine, crystallised from benzene in colourless needles which darkened at 145° and melted at 152° with inflation [Found: Br, 47·3 (Stepanoff). $C_{21}H_{22}O_5Br_4$ requires Br, 47·4%].

Ethyl 3-mp-*Dimethoxyphenyl*-5-mp-*dimethoxystyryl*-Δ^5-cyclo*hexen*-1-*one*-2-*carboxylate* (III).—A solution of 3 : 3′ : 4 : 4′-tetramethoxydistyryl ketone (10 g.) and ethyl acetoacetate (4 g.) in boiling alcohol (75 c.c.) was treated with sodium ethoxide (0·4 g. of sodium in 25 c.c. of alcohol) and maintained at the boiling point for 5 minutes. The crystalline solid which separated on cooling (yield, above 90%) was twice recrystallised from absolute alcohol, in which it was sparingly soluble, giving bright yellow needles, m. p. 160—161° (Found: C, 69·3; H, 6·5. $C_{27}H_{30}O_7$ requires C, 69·5; H, 6·4%).

3-mp-*Dimethoxyphenyl*-5-mp-*dimethoxystyryl*-Δ^5-cyclo*hexen*-1-*one* (II).—The above-mentioned ester (5 g.), dissolved in glacial acetic acid (75 c.c.), was boiled with 20% sulphuric acid (50 c.c.) under reflux for 4 hours. After cooling, the dark red liquid was slowly poured into ice-water (1000 c.c.). The greenish-yellow, curdy precipitate was crystallised from alcohol and then twice from ethyl acetate. The cyclo*hexenone* formed minute, pale yellow

needles, m. p. 168°, which tenaciously retained traces of ethyl acetate. For analysis, the substance was heated in a vacuum at 100° for several hours. It readily absorbed two molecules of bromine, but no pure bromo-derivative could be isolated (Found: C, 73·0; H, 6·4. $C_{24}H_{26}O_5$ requires C, 73·1; H, 6·6%).

The direct preparation of 3-*mp*-dimethoxyphenyl-5-*mp*-dimethoxystyryl-Δ^5-*cyclo*hexen-1-one was carried out by the following modification of Francesconi and Cusmano's method (*loc. cit.*). Veratraldehyde (12 g.), dissolved in aqueous acetone (70 c.c.), was treated with sodium hydroxide solution (25 c.c. of 1%). After the mixture had been kept for 2 days in the ice-chest, the solid was separated and twice recrystallised from ethyl acetate; the pure product, m. p. 168°, was then obtained (yield 20%). The filtrate gave on dilution a viscous yellow oil, from which a small quantity of the normal monostyryl ketone (m. p. 85°) was isolated. The compound, m. p. 168°, gave no depression in melting point in admixture with the *cyclo*hexenone prepared as described above, the constitution of which is definitely determined. The *cyclo*hexenone was also prepared by keeping an acetone solution of 3:4-dimethoxystyryl methyl ketone, mixed with a few drops of 8% sodium hydroxide solution, at room temperature for several days. The solution slowly darkened and deposited a crystalline, yellow mass which, after recrystallisation from ethyl acetate, was identical with the Francesconi compound (Found: C, 73·1; H, 6·6%; *M*, 396, 395). Both substances were mixed with the synthesised *cyclo*hexenone (II), but no depression in melting point was noted.

Preparation of the cyclo*hexenone semicarbazone.* A solution of the *cyclo*hexenone (2 g.) in glacial acetic acid was treated with semicarbazide acetate. The yellow solution slowly became red and after 3 days the separated solid was filtered off, washed with water, and dried. On boiling with alcohol part dissolved and part was converted into a golden-yellow, crystalline powder; an identical product was obtained from the alcoholic solution. The *monosemicarbazone* forms golden-yellow rhombs, m. p. 226—227° to a red liquid, and regenerates the *cyclo*hexenone on being refluxed with aqueous-alcoholic oxalic acid for several hours (Found: N, 9·2. $C_{25}H_{29}O_5N_3$ requires N, 9·3%).

Dimeride of 3:4-*Dimethoxystyryl Methyl Ketone.*—3:4-Dimethoxystyryl methyl ketone (20 g.) was heated on a steam-bath with piperidine (30 c.c.) for 24 hours. The solution was diluted with water and acidified, and the resinous precipitate obtained, on repeated treatment with boiling alcohol, yielded a white, amorphous powder. For analysis, the compound, which was obtained only

in very small yield, was precipitated from benzene solution by the gradual addition of light petroleum; m. p. 209—210° (Found: C, 70·2; H, 6·7; *M*, 418. $C_{24}H_{28}O_6$ requires C, 69·9; H, 6·8%; *M*, 412).

3-*Methoxy*-4-*ethoxystyryl Methyl Ketone*.—Ethylvanillin (5 g.), prepared according to Tiemann's method (*Ber.*, 1875, **8**, 1129), was dissolved in alcohol (5 c.c.) and acetone (15 c.c.) and treated with 1% sodium hydroxide solution (20 c.c.). After an hour, a yellow oil commenced to separate which only very slowly became solid. In subsequent experiments, seeding the mixture at this stage brought about a rapid separation of the solid ketone. Recrystallised from dilute alcohol, it formed yellow needles, m. p. 106° (yield, 83%). The ketone was also obtained in a colourless modification having the same melting point by allowing the yellow modification to stand in suspension in water or xylene for several weeks in direct sunlight. Whereas the yellow form gives an intense crimson coloration in concentrated hydrochloric acid, the colourless isomeride dissolves to a yellow solution (Found: C, 70·7; H, 7·0; *M*, 236. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%; *M*, 220). The *semicarbazone* separates from alcohol in pale yellow plates, m. p. 208—209° (Found: N, 15·4. $C_{14}H_{19}O_3N_3$ requires N, 15·2%).

3 : 3′-*Dimethoxy*-4 : 4′-*diethoxydistyryl Ketone*.—Ethylvanillin (5 g.) and acetone (1 c.c.) were dissolved in 50% alcohol (100 c.c.) together with 10% sodium hydroxide solution (2·5 c.c.) and the mixture was left at room temperature for 24 hours. The yellow precipitate was recrystallised from alcohol, the pure *ketone* separating in yellow needles, m. p. 123—124° (yield, 50%) (Found: C, 72·0; H, 6·8. $C_{23}H_{26}O_5$ requires C, 72·2; H, 6·8%).

Dimeride of 3-*Methoxy*-4-*ethoxystyryl Methyl Ketone*.—The styryl ketone (19 g.) was refluxed on a steam-bath with piperidine (30 c.c.) for 24 hours. The gummy precipitate formed on addition of water was repeatedly washed with alcohol, whereby resinous impurities were wholly removed. The polymeride was purified by slow precipitation from benzene solution by means of light petroleum. It formed a white, amorphous powder, m. p. 187° (yield, 5%) (Found: C, 70·9; H, 7·4; *M*, 446, 465. $C_{26}H_{32}O_6$ requires C, 70·9; H, 7·3%; *M*, 440).

Propylvanillin.—A mixture containing the potassium salt of vanillin (19 g.), propyl iodide (25 g.), and absolute alcohol (20 c.c.) was heated for 12 hours under reflux on the water-bath. After removal of part of the alcohol, the residue was poured into water; the precipitated oil rapidly solidified. This was dissolved in ether and repeatedly washed with dilute alkali solution to remove unchanged vanillin. The residue left after removal of the ether was

recrystallised from dilute alcohol, *propylvanillin* being obtained in colourless crystals, m. p. 59—60° (yield, 60%) (Found: C, 67·8; H, 7·4. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·2%). The *semicarbazone* separated from alcohol in colourless needles, m. p. 156° (Found: N, 16·9. $C_{12}H_{17}O_2N_3$ requires N, 16·7%).

3-*Methoxy*-4-*propoxystyryl Methyl Ketone.*—A solution of propylvanillin (2 g.) in acetone (8 c.c.) and alcohol (3 c.c.) was treated with 1% aqueous sodium hydroxide (8 c.c.). The product, which rapidly separated, was twice recrystallised from alcohol, the pure styryl ketone forming bright yellow rhombs, m. p. 92—93° (Found: C, 71·9; H, 7·8. $C_{14}H_{18}O_3$ requires C, 71·8; H, 7·7%).

3-m-*Methoxy*-p-*propoxyphenyl*-5-m-*methoxy*-p-*propoxystyryl*-Δ^5-cyclo*hexen*-1-*one.*—The ketone (10 g.) in acetone (75 c.c.), alcohol (50 c.c.), and water (100 c.c.) was treated with 2*N*-sodium hydroxide (10 c.c.), and the whole left at room temperature for 3 days. The small amount of yellow precipitate crystallised from ethyl acetate in pale yellow needles, m. p. 152—153°. It readily absorbed two molecules of bromine, halochromic colour effects being shown, but no solid tetrabromide could be isolated (Found: C, 74·5; H, 7·6. $C_{28}H_{34}O_5$ requires C, 74·7; H, 7·6%).

iso*Propylvanillin*, prepared in the same way as the *n*-isomeride, formed a pale yellow, viscous liquid, b. p. 150—152°/13 mm. The *semicarbazone* separated from alcohol in colourless needles, m. p. 151—152° (Found: N, 16·6. $C_{12}H_{17}O_3N_3$ requires N, 16·7%).

3-*Methoxy*-4-iso*propoxystyryl methyl ketone*, prepared by the method described for the *n*-isomeride, separated as a yellow oil which only became solid after long standing. It crystallised from aqueous alcohol in yellow flakes, m. p. 51—53°. An acetone–alcoholic solution of the ketone in presence of alkali darkened fairly rapidly, but only resinous material was isolated. The *semicarbazone* formed yellow needles, m. p. 203—204° (Found: N, 14·6. $C_{15}H_{21}O_3N_3$ requires N, 14·4%).

Benzylvanillin, previously prepared by the oxidation of benzyl-*iso*eugenol (Boehringer und Söhne, D.R.-P. 65,937, 1891), is more conveniently prepared by the following method. A thin alcoholic paste of the potassium salt of vanillin (23 g.) was heated under reflux with benzyl chloride (25 g.) for 12 hours. The excess of benzyl chloride was removed by short distillation in steam and the residual oil, which solidified on cooling, was twice recrystallised from alcohol, benzylvanillin being obtained in colourless crystals, m. p. 64—65° (yield, 70%).

3-*Methoxy*-4-*benzyloxystyryl Methyl Ketone.*—A solution of benzylvanillin (5 g.) in acetone (8 c.c.) and alcohol (20 c.c.) was treated

with sodium hydroxide solution (8 c.c. of 0·5%) and kept in the ice-chest; an oil then separated which slowly solidified. The crude product (yield, 80%) contained a small amount of the corresponding distyryl ketone, which was only separated with difficulty by fractional crystallisation either from alcohol or ethyl acetate. The *ketone* crystallised from alcohol in yellow needles, m. p. 93° (Found: C, 76·4; H, 6·4; *M*, 280, 285. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%; *M*, 282). The *semicarbazone* formed a yellow powder, m. p. 200—201° (Found: N, 12·4. $C_{19}H_{21}O_3N_3$ requires N, 12·4%).

3 : 3′-*Dimethoxy*-4 : 4′-*dibenzyloxydistyryl Ketone.*—A solution of benzylvanillin (2 g.) in acetone (0·5 c.c.) and alcohol (30 c.c.) was treated with 1% sodium hydroxide solution (10 c.c.). After 24 hours, the mixture was neutralised with dilute acetic acid, whereupon an oil separated which rapidly solidified. The distyryl ketone crystallised from ethyl acetate in golden-yellow needles, m. p. 155°. Alternatively, the same compound may be obtained by condensation of 3-methoxy-4-benzyloxystyryl methyl ketone with benzylvanillin (Found: C, 78·1; H, 6·0. $C_{33}H_{30}O_5$ requires C, 78·3; H, 5·9%). The *tetrabromide*, obtained by treating the ketone in chloroform solution with the calculated amount of bromine, formed minute, colourless needles, m. p. 141° (decomp.), from benzene. This compound rapidly decomposes with loss of bromine.

An apparent isomeride of this distyryl ketone was isolated in an attempt to prepare the *cyclo*hexenone from 3-methoxy-4-benzyloxystyryl methyl ketone by the action of alkali in the following manner. The monostyryl ketone (10 g.) in acetone (36 c.c.) and alcohol (36 c.c.) was treated with 8% sodium hydroxide solution (25 c.c.), and the mixture was kept at room temperature for 6 hours and in the ice-chest for 2 days. A solid separated which, after three recrystallisations from ethyl acetate, was obtained in dark orange-yellow needles, m. p. 174—175°. This substance absorbs 2 molecules of bromine, but no solid bromide could be isolated (Found: C, 78·3; H, 6·2%).

Phenyl 3 : 4-*Dimethoxystyryl Ketone.*—A solution of veratraldehyde (5·6 g.) and acetophenone (4 g.) in alcohol (30 c.c.) was treated with 10% sodium hydroxide solution (12 c.c.). After an hour, an oil separated which slowly solidified; in subsequent experiments, seeding of the oil brought about almost instantaneous solidification. The chalkone separated from aqueous alcohol in yellow needles, m. p. 88° (yield, 70%) (Found: C, 75·9; H, 6·3. $C_{17}H_{16}O_3$ requires C, 76·1; H, 6·0%). Attempts to condense this compound to a *cyclo*hexenone by means of alkali failed, only resinous material being formed.

In conclusion, we desire to express our thanks to the Council of the Department of Scientific and Industrial Research for a grant to one of us (R. D.) and also to the Cumberland County Council for the renewal of a scholarship (F. I.) which has enabled this research to be carried out.

THE UNIVERSITY, LIVERPOOL. [*Received, June 8th*, 1927.]

CCXLIV.—*The Oxidation of* n-*Triacontane.*

By FRANCIS FRANCIS and NORMAN EDWARD WOOD.

IT is now known that Scotch paraffin wax fusing between 55° and 56°, and probably all similar waxes, are composed of ten to twelve *n*-hydrocarbons (J., 1926, 1420).

The oxidation of paraffin by air or oxygen has been described in this Journal, but in 1922 (J., **121**, 501) it was shown that the synthetic hydrocarbons *n*-hexadecane and *n*-dotriacontane in the presence of 5% of turpentine suffered no change when treated with a current of air at 100° for 730 and 696 hours, respectively. Under similar conditions, paraffin wax reached a content of about 19% of oxygen. At that time, these observations led to the conclusion that the hydrocarbons present in the latter substance differed from those of the normal series.

Later it was found, however, that the presence of very small quantities of certain impurities in paraffin was capable of greatly prolonging the latent phase of the oxidation process, that characteristic period in this reaction when no change is observed.

Both of the above hydrocarbons had been synthesised from their halogen derivatives—octyl and cetyl iodide—purified by the ordinary method, and were judged from their constants and analyses to be pure. A sufficient amount of the specimen of hexadecane used in the work was available, and on being tested was found to contain traces of iodine, and there is but little doubt that the dotriacontane was contaminated in a similar manner. It was highly probable that these impurities had prolonged the latent period of the oxidation, and in order to test this view, a suitable hydrocarbon—*n*-triacontane—was synthesised by a method that did not involve the use of halogen derivatives.

Triacontane was prepared by the electrolysis of potassium palmitate (Peterson, *Z. Elektrochem.*, 1906, **12**, 141). The palmitic acid used was Kahlbaum's purest preparation, and the resulting hydrocarbon (480 g.) was purified by crystallisation from benzene, followed by fractional distillation in a vacuum. It fused at 66·5°, and boiled at 304° (corr.)/15 mm.; the analysis is given in Table I.

During this preparation, about 70 g. of a hydrocarbon were isolated, liquid at the ordinary temperature, a description of which will be given in a later communication.

When triacontane and 5% of turpentine were treated at 95° ± 2° with a current of air free from moisture and carbon dioxide, oxidation took place in a manner strikingly similar to that shown by paraffin wax or the hydrocarbons isolated from it. The analysis of the material after the passage of air for various periods is given in Table I, *a* being the duration of the air current in hours. The final product showed an acid value of 88·6.

TABLE I.

Oxidation of $C_{30}H_{62}$. $t = 95° \pm 2°$.

a.	% C.	% H.	% O by diff.	*a*.	% C.	% H.	% O by diff.
Hydrocarbon	84·9	14·9	—	506	80·5	13·6	5·9
173	82·5	14·5	3·0	577	79·1	13·0	7·9
266	82·4	14·5	3·1	748	78·0	12·8	9·2
341	82·3	14·3	3·4	865	76·1	12·6	11·3
413	81·3	14·0	4·7	1009	75·7	12·2	12·1

If the data in Table I be compared with those for paraffin wax at 100° (J., 1924, **125**, 387), it will be seen that in both cases there is a halt in the progress of the oxidation when the oxidised material contains about 3% of oxygen, and a similar but less well-marked phenomenon when the content has reached 8% of this element.

With the above hydrocarbon at the temperature mentioned, an oxygen content of 7% is reached in 550 hours; at 100°, paraffin wax requires 790 hours, the hydrocarbon $C_{22}H_{46}$ isolated from paraffin 460 hours, and $C_{29}H_{60}$ from the same source 420 hours (compare J., 1924, **125**, 383).

Products of the Oxidation.—(1) During the oxidation of paraffin wax, of the hydrocarbons isolated from it, and of triacontane itself, carbon dioxide and formic acid are formed. The amounts of these were determined by passing the gases through an excess of barium hydroxide solution. Triacontane gave 4·3 g. of carbon dioxide per 100 g. of hydrocarbon oxidised, and in the other cases the amount varied between 4·6 and 6·3 g. The amount of carbon in the form of formic acid produced from triacontane was 0·6 g. per 100 g. oxidised, and in the other cases varied between 1·0 and 1·3 g.

(2) The products of the oxidation were freed from unoxidised triacontane by several crystallisations from fifteen times the volume of acetone. The unchanged hydrocarbon, insoluble in this solvent, amounted to 21%. In the case of paraffin wax under comparable conditions, the corresponding amount lies between 25 and 30%.

(3) The oxidised triacontane, consisting of acids and inert material, was then saponified with an alcoholic solution of caustic potash, water added until 50% was present, and the inert products were extracted with large quantities of light petroleum. The acids amounted to 64%, whereas in the case of paraffin wax they lay between 58 and 69% in different experiments.

Acidic Products of the Oxidation.—(1) The acids were steam-distilled, but the amount of oily distillate was too small for identification. The water in the distilling flask, however, had dissolved a small quantity of a substance which consisted chiefly of succinic acid, although the amount isolated was insufficient for complete purification. It fused at 176°, and at 178—179° when mixed with succinic acid (m. p. 181°), and its molecular weight by titration was 119 (Found: C, 41·2; H, 4·3. Calc. for $C_4H_6O_4$: C, 40·7; H, 5·1%; *M*, 118).

(2) The cake of dry acids from the previous operation was recrystallised several times from chloroform followed by acetone, and about 9% of a mixture of white, crystalline acids was obtained. After long-continued fractional crystallisation, these were found to consist chiefly of $C_{26}H_{52}O_2$, which appeared to be identical with cerotic acid, and a small quantity of $C_{24}H_{48}O_2$. Both these acids had been previously isolated in this laboratory from products of the oxidation of paraffin wax.

The specimen of cerotic acid used for the comparison was prepared for us by the Eastman Kodak Co. It had been isolated from beeswax and purified by the fractionation of its methyl ester. Both this acid and the corresponding one mentioned above were further purified by conversion, in methyl-alcoholic solution, into the barium salt, which was extracted with ether and finally with acetone. The acids recovered from these salts by solution in hot acetic acid were repeatedly crystallised from acetone and finally from light petroleum. The full comparison is given in Table II.

The data given for the corresponding acids from paraffin wax (*a*) and (*b*) were for specimens isolated by different observers and their preparation will be described in another communication. We have to thank Mr. Piper, who is undertaking an investigation of these other acids, for the *X*-ray data. He informs us that, as regards the high values in the above table, the error is about 1%. We point out that the melting points of the above acids are about 10° lower than that of the synthetic acid of the same carbon content, which, according to Levene and Taylor, fuses at 88·5° (*J. Biol. Chem.*, 1924, **59**, 919). We leave to a later date the discussion of this acid and that melting at 74°, of acid value 152, which is probably $C_{24}H_{48}O_2$, together with a series of what are believed to be

TABLE II.

Source.	Beeswax.	$C_{30}H_{62}$.	Paraffin wax. (*a*).	Paraffin wax. (*b*).
M. p.	77·5°	78°	80°	76°
Mixed m. p.	77·5—78°			
Acid value. (Calc. for $C_{26}H_{52}O_2$, 141)	144	145	141	146
Calc. for $C_{26}H_{52}O_2$ { C 78·8%	78·6%	78·4%	79·1%	78·9%
Calc. for $C_{26}H_{52}O_2$ { H 13·1%	13·1%	13·2%	13·3%	13·1%
X-Ray spacing, "pressed." Å.	68·03	68·85	68·8	68·4
M. p. of methyl ester. (Previous observers, 60—62°)	60·5°	63·5°	62—3°	62°
Mixed m. p.	62°			
M. p. of ethyl ester. (Previous observers, 59—60°)	58°	60·5°		
Mixed m. p.	59°			
X-Ray spacing, "pressed." Å. Ethyl ester.	39·15	39·0		

analogous acids, which have been isolated from the oxidation products of paraffin wax.

(3) The main bulk of the acids, from which cerotic acid and the acid $C_{24}H_{48}O_2$ have been removed, is a complex mixture of monobasic and oxy-acids which cannot be separated from the small amount of inert material present by conversion into barium salts and extraction with solvents. The mixture is as difficult to deal with as that of the corresponding material from paraffin wax.

The material was converted into methyl esters, of which about 38% could be distilled without decomposition in a vacuum of 3 mm., this amount corresponding closely with that observed in the case of the similar complex obtained from paraffin wax. The distillate boiled between 140° and 205°/6 mm. and on standing in the ice-chest deposited a crystalline substance. The acids obtained from this were fractionally crystallised from acetone and finally two were isolated in small quantities: (A) M. p. 63°, acid value 188. Found: C, 76·1, 76·3; H, 12·7, 12·7%. The pressed *X*-ray spacings were Å. 52·11. Provisionally this is regarded as $C_{20}H_{40}O_2$ (Calc.: Acid value, 179; C, 76·9; H, 12·8%). (B) M. p. 53·4°. Found: C, 74·8, 75·0; H, 12·5, 12·4%. The pressed *X*-ray spacings = Å. 46·56. This is provisionally regarded as $C_{16}H_{32}O_2$ (Calc.: C, 75·0; H, 12·5%), but is probably contaminated with an acid of higher carbon content.

(4) The residue of esters which could not be distilled gave a

small quantity of an acid, fusing at 68° after repeated crystallisation from glacial acetic acid (Found: C, 76·9; H, 12·6%). It is probably an impure specimen of $C_{22}H_{44}O_2$ (Calc.: C, 77·6; H, 12·9%).

Acids similar to those just described have been isolated in larger quantities from the products of the oxidation of paraffin wax.

Inert Products of the Oxidation.—Following the method previously described (J., 1926, 2377), the non-acidic products of the oxidation were repeatedly crystallised from five times their weight of acetone, and thus separated into a relatively insoluble, white, crystalline mass, comprised chiefly of ketones and dioxy-products constituting together about 46% of the mixture, and a more soluble coloured mixture of more highly oxidised hydrocarbon, which was not further examined.

(i) The crystalline mixture fused at 58—59°. It was acetylated and the more soluble acetyl derivatives were separated by their greater solubility in acetone. The acetates were decomposed, and the resulting alcohol after purification fused at 69° (Found: C, 79·4; H, 13·5. Calc. for $C_{30}H_{60}O_2$: C, 79·6; H, 13·2%). It was either a ketonic alcohol or a dihydroxy-derivative, but the amount obtained was insufficient for further examination. The residual material, from which a certain part of the dioxy-substance had been separated, fused at 60—61° and contained C, 80·7; H, 14·2%. It was chiefly composed of ketones and dioxy-derivatives.

(ii) This mixture was treated with hydroxylamine, and the resulting oxime separated by its greater solubility in alcohol from the other substances present. The oxime itself could not be purified, but on saponification it gave a well-defined, crystalline ketone, m. p. 62·5° (Found: C, 82·0; H, 13·8. Calc. for $C_{30}H_{60}O$: C, 82·5; H, 13·7%).

Mr. Piper examined this specimen by *X*-rays and informed us that it contained 30 carbon atoms and, judging from the intensity distribution, the oxygen was situated most probably on the fourth carbon atom. (See J., 1926, 2381, for corresponding ketones with lower carbon content obtained from paraffin wax.)

Summary.

We have shown the striking similarity between the oxidation of synthetic triacontane, the mixture of solid *n*-hydrocarbons termed paraffin wax, and the pure constituents isolated from the latter. This similarity extends, not only to the velocity of oxidation, but to the nature and amounts of the products formed.

The highest acid present among the acidic products of the oxidation of triacontane has a carbon content of 26 atoms and appears to be identical with cerotic acid obtained from beeswax. This

acid fuses 10° lower than the corresponding synthetic acid, a phenomenon noticed with other acids obtained from paraffin wax, which will be discussed at a later date.

Support has been obtained for the view expressed previously (J., 1926, 2383) that in the oxidation of hydrocarbons such as triacontane the first product is a secondary alcohol, which then passes to a ketone. The latter has been isolated and found to have a carbon content of 30 atoms. *X*-Ray analysis indicates that the oxygen is situated on the fourth carbon atom; on further oxidation, the chain breaks, and the fact that a C_{26} acid results leads to the conclusion that the ketone has the structure

$$CH_3 \cdot [CH_2]_{24} \cdot CH_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_3.$$

This view is also supported by the presence of succinic acid among the products of the reaction.

The amount of acids with high carbon content resulting from the oxidation of such long-chain hydrocarbons is always very small. Probably, simultaneously with the formation of the secondary alcohol followed by that of the ketone and their breakdown into acids, there occurs the further oxidation of the mono-oxy-derivative first formed to polyhydroxy-derivatives, which on further oxidation pass to ketones and then break down to acids and oxy-acids of still smaller carbon content.

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UNIVERSITY OF BRISTOL. [*Received, June 1st*, 1927.]

CCXLV.—*The Isomeric Hydroxybenzyldimethylamines.*

By EDGAR STEDMAN.

A SEPARATE problem necessitated the synthesis of the isomeric hydroxybenzyldimethylamines, which was effected by treating the methoxybenzyl bromides with dimethylamine and hydrolysing the methoxybenzyldimethylamines so prepared with hydrobromic acid —a method similar to that employed by Tiffeneau (*Bull. Soc. chim.*, 1911, **9**, 825) for the preparation of the *p*-isomeride. Previous unsuccessful attempts had been made to prepare these phenols from the nitrobenzyl chlorides. Dimethylamine converted the latter into the nitrobenzyldimethylamines, which, on reduction, gave the aminobenzyldimethylamines. These underwent smooth diazotisation, but no phenol could be isolated from the tarry product obtained by decomposing the diazo-compound in hot aqueous solution.

In the interaction between *p*-nitrobenzyl chloride and dimethylamine, a considerable quantity of di-*p*-nitrobenzyldimethylammonium chloride was produced, whilst only insignificant amounts (if any) of such quaternary salts were formed from the *o*- and *m*-isomerides. Although the reactions were not carried out under the same conditions of concentration, this result agrees with the recent experiments of McCombie, Scarborough, and Smith (this vol., p. 802), who have shown that the velocity coefficient for the formation of quaternary salts from trimethylamine and the nitrobenzyl chlorides is greater in the case of the *p*- than of the *o*- and *m*-isomerides.

EXPERIMENTAL.

o-, m-, *and* p-*Hydroxybenzyldimethylamine.*—A solution of the methoxybenzylbromide in benzene was prepared by saturating a benzene solution of the methoxybenzyl alcohol with dry hydrogen bromide, drying it over anhydrous calcium bromide, and distilling off benzene until most of the excess hydrobromic acid had been removed (compare Lapworth and Shoesmith, J., 1922, **121**, 1391). Excess of a solution of dimethylamine in benzene was then added and after 24 hours the dimethylamine bromide which had separated was removed by filtration and the methoxybenzyldimethylamine extracted from the benzene solution with hydrochloric acid. Traces of benzene were removed from the acid solution by extraction with ether, and the base was liberated with sodium hydroxide and extracted with ether. Evaporation of the dried ethereal extract gave the methoxybenzyldimethylamine, which, after being distilled under diminished pressure, was converted into the hydroxybenzyldimethylamine by boiling with constant-boiling hydrobromic acid. In the case of the *m*-compound, 4 hours sufficed completely to hydrolyse the methoxy-group. The hydrobromic acid was removed by distillation under diminished pressure, the residue dissolved in water and made alkaline with sodium carbonate, and the phenol shaken out with ether. The product obtained on evaporation of the dried ethereal extract rapidly crystallised. In the case of the *o*- and *p*- compounds, the treatment with hydrobromic acid was continued for 10 hours. Nevertheless, hydrolysis was incomplete and considerable decomposition occurred with the *p*-isomeride. In both cases, the product left after removal of the hydrobromic acid was dissolved in water, and the solution was extracted with ether before and after being made alkaline with sodium hydroxide in order to remove impurities and unchanged methoxy-compound. It was then made slightly acid and the phenol was precipitated with sodium carbonate and shaken out with ether. Evaporation of the dried ethereal extract gave the phenols in fairly pure form.

m-*Methoxybenzyldimethylamine* is a colourless oil, b. p. 105°/13 mm. The *hydrochloride* crystallises from acetone–alcohol in tablets, m. p. 173° (Found: Cl, 17·6. $C_{10}H_{15}ON,HCl$ requires Cl, 17·6%).

m-*Hydroxybenzyldimethylamine* crystallises from benzene in prisms, m. p. 108°. The *hydrochloride* crystallises from alcohol in flat prisms, m. p. 173° (Found: Cl, 18·9. $C_9H_{13}ON,HCl$ requires Cl, 18·9%).

p-Methoxybenzyldimethylamine has b. p. 109°/13 mm. (compare Tiffeneau, *loc. cit.*). The *hydrochloride* crystallises from acetone in prisms, m. p. 152° (Found: Cl, 17·6%).

p-Hydroxybenzyldimethylamine (compare Tiffeneau) has m. p. 106°. The *hydrochloride* separates from alcohol in macroscopic prisms, m. p. 185° (Found: Cl, 18·7%).

o-*Methoxybenzyldimethylamine* is a colourless oil, b. p. 113°/20 mm. The *hydrochloride* is hygroscopic. After crystallisation from acetone, it has m. p. 149° (Found: Cl, 17·7%).

o-*Hydroxybenzyldimethylamine* is a colourless oil, b. p. 99–100°/12 mm. The *methiodide* crystallises from alcohol in prisms, m. p. 169° (Found: I, 43·1. $C_9H_{13}ON,CH_3I$ requires I, 43·35%).

o-*Nitrobenzyldimethylamine*.—An alcoholic solution of 30 g. of *o*-nitrobenzyl chloride was treated with dimethylamine (slightly more than 2 mols.) dissolved in the same solvent. After 3 days, the alcohol was evaporated, and the residue treated with water and sufficient hydrochloric acid to produce a clear solution. After extraction with ether to remove any unchanged nitrobenzyl chloride, the solution was made alkaline with sodium carbonate and the oil thus precipitated shaken out with ether. Evaporation of the dried ethereal extract left 29·1 g. of an oil. This was converted directly into the hydrochloride (yield 33 g.). When recrystallised from alcohol–acetone, the *hydrochloride* of o-*nitrobenzyldimethylamine* forms long, almost colourless prisms, m. p. about 221° (Found: Cl, 16·4. $C_9H_{12}O_2N_2,HCl$ requires Cl, 16·4%).

o-*Aminobenzyldimethylamine*.—The hydrochloride (10 g.) of *o*-nitrobenzyldimethylamine was mixed with 17 g. of granulated tin, and 70 g. of concentrated hydrochloric acid were added slowly in small portions, with efficient cooling. The solution was finally heated on the water-bath for 30 minutes and then cooled. The crystalline stannichloride which had separated was filtered off and decomposed in aqueous solution by hydrogen sulphide, the filtrate from the tin sulphide was boiled to expel the excess of hydrogen sulphide and made alkaline with sodium carbonate, and the oil thus precipitated was extracted with ether. Evaporation of the dried ethereal extract left 4 g. of a somewhat brown oil which slowly crystallised. (A further 1·6 g. was obtained by working up

the filtrate from the stannichloride in a similar manner.) This was distilled under diminished pressure; o-*aminobenzyldimethylamine*, b. p. 107°/14 mm., then passed over as a colourless oil which crystallised completely on cooling. The crystals had m. p. 36—37°. The *dihydrochloride* separates from alcohol in blunt prisms, m. p. 205° after sintering at 193° (Found: Cl, 31·7. $C_9H_{14}N_2,2HCl$ requires Cl, 31·8%).

Action of Dimethylamine on p-*Nitrobenzyl Chloride.*—A mixture of dimethylamine (slightly more than 2 mols.) and *p*-nitrobenzyl chloride (30 g.) in alcoholic solution was kept for 3 days. The alcohol was then evaporated, and the residual brown oil treated with water and sufficient hydrochloric acid to produce a clear solution. Ether extracted from this a small quantity of a red oil. Addition of sodium carbonate to the aqueous solution precipitated an oil which partly solidified. Extraction with ether removed the oil, but not the solid. On evaporation of the dried ethereal extract, an orange oil (20·8 g.) was obtained. This was converted directly into the hydrochloride, but only 14 g. could be obtained in solid form. The *hydrochloride* of *p*-nitrobenzyldimethylamine thus prepared crystallised from acetone–alcohol in faintly yellow plates, m. p. 188° (Found: Cl, 16·3. $C_9H_{12}O_2N_2,HCl$ requires Cl, 16·4%). The base was recovered from the oily residue from the preparation of the hydrochloride and divided into two portions, one of which was treated with methyl iodide. This yielded p-*nitrobenzyltrimethylammonium iodide*, which crystallised from alcohol in yellow, wedge-shaped prisms, m. p. 198° (Found: I, 39·1. $C_9H_{12}O_2N_2,CH_3I$ requires I, 39·4%). The second portion of the recovered base was treated with an alcoholic solution of oxalic acid; the *oxalate* of *p*-nitrobenzyldimethylamine was thus obtained, which separated from alcohol in lustrous, yellow plates, m. p. 155°. The identities of the oxalate and methiodide were established by recovering the base from the oxalate and converting separate portions into its methiodide and hydrochloride. The salts obtained were identical with those described above.

The above-mentioned solid which was not extractable with ether was filtered off (yield 8·8 g.) and recrystallised from alcohol; it then formed stout prisms, m. p. about 176°. Its behaviour was that of a quaternary chloride, for it was soluble in water and its aqueous solution contained ionic chlorine, but gave no precipitate on addition of alkalis. Analysis indicated that it was *di*-p-*nitrobenzyldimethylammonium chloride* (Found: Cl, 10·1. $C_{16}H_{18}O_4N_3Cl$ requires Cl, 9·8%).

p-Aminobenzyldimethylamine, prepared as in the case of the *m*-isomeride, has b. p. 133°/16 mm. (compare Friedländer and

Mosczyc, *Ber.*, 1895, **28**, 1141). The *dihydrochloride* separates from alcohol in needles, m. p. 216° (Found: Cl, 31·7. $C_9H_{14}N_2,2HCl$ requires Cl, 31·8%).

m-*Nitrobenzyldimethylamine* was prepared from *m*-nitrobenzyl chloride (20 g.) and dimethylamine as in the case of the *o*-isomeride, 19·1 g. of a yellow oil being obtained. This was converted directly into the hydrochloride (yield 23 g.). When recrystallised from alcohol, the *hydrochloride* of *m*-nitrobenzyldimethylamine forms practically colourless, stout prisms, m. p. 230° (Found: Cl, 16·3. $C_9H_{12}O_2N_2,HCl$ requires Cl, 16·4%).

m-*Aminobenzyldimethylamine* was prepared by the method employed for the *o*-isomeride. 10 G. of the hydrochloride of the nitro-compound yielded a crystalline stannichloride which, on decomposition with hydrogen sulphide, gave 3 g. of the base. On distillation, it was obtained as a colourless oil, b. p. 129°/13 mm., which rapidly crystallised. The crystals had m. p. 46°. The *dihydrochloride* crystallised from alcohol in prisms, m. p. 225° after sintering at 210° (Found: Cl, 31·7. $C_9H_{14}N_2,2HCl$ requires Cl, 31·8%).

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DEPARTMENT OF MEDICAL CHEMISTRY,
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CCXLVI.—*The Effect of Hydrochloric Acid on the Electrode Potential between Mercury and Mercurous Chloride.*

By SYDNEY RAYMOND CARTER, FREDERICK MEASHAM LEA, and ROBERT ANTHONY ROBINSON.

THE effect of hydrochloric acid on the electrode potential between mercury and calomel has been investigated by Sauer (*Z. physikal. Chem.*, 1904, **47**, 146), who worked with 0·1*N*- and 1·0*N*-solutions of hydrochloric acid. Measurements have also been made by Tolman and Ferguson (*J. Amer. Chem. Soc.*, 1912, **34**, 232), Ellis (*ibid.*, 1916, **38**, 737), and Linhart (*ibid.*, 1917, **39**, 2601), on cells of the type:

$$H_2|xN\text{-HCl, solid } Hg_2Cl_2|Hg$$

combined with a similar cell using *N*-hydrochloric acid, the whole forming a concentration cell without transport, reversible with respect to both the chlorine and the hydrogen ions.

Direct measurements of cells of the type :

$$Hg|Hg_2Cl_2,xN\text{-}HCl|N\text{-}HCl|N\text{-}KCl|N\text{-}KCl,Hg_2Cl_2|Hg$$

have now been carried out, a correction being applied for the diffusion potential across the boundary xN-HCl|N-HCl on the basis of some earlier results (Carter and Lea, J., 1925, **127**, 487). Measurements of this type have been employed to elucidate certain results which are described in the succeeding communication.

Construction of Cells.—Mercurous chloride was obtained in a state of purity, containing no mercuric chloride and only a trace of free mercury. The mercury used was purified both by electrolytic methods and by distillation. Cell solutions were prepared by grinding calomel, together with a little free mercury, into a paste with hydrochloric acid of a known concentration. The supernatant liquid was decanted repeatedly as in the construction of the normal calomel electrode. The electrode was of mercury, and upon this was placed a thin layer of calomel paste, the vessel being filled with hydrochloric acid solution saturated with calomel. The following chain of solutions was constructed :

$$\underset{E}{\overleftarrow{Hg|Hg_2Cl_2,xN\text{-}HCl}}|\underset{\pi}{\overset{A}{\rightarrow}}xN\text{-}HCl|\underset{0\cdot0288}{\overset{B}{\rightarrow}}N\text{-}HCl|N\text{-}KCl|N\text{-}KCl,\underset{0\cdot560}{\overrightarrow{Hg_2Cl_2|Hg}}$$

$$\xleftarrow[E_c]{}$$

Special experiments were made in order to ascertain that the diffusion potentials were constant over a considerable period of time and were also reproducible. Several arrangements were tried, but the above was found to be the most satisfactory. Connexion between the solutions at A and B was made by means of inverted U-tubes filled with N-solutions of hydrochloric acid and potassium chloride, respectively, and plugged at both ends with wads of filter paper. The diffusion potential at B can be calculated on the basis of Henderson's formula (*Z. physikal. Chem.*, 1907, **59**, 118) to be 0·0288 volt. That at A has been measured (Carter and Lea, *loc. cit.*) for values of x greater than unity; for values less than unity it may be calculated from the usual formula. Thus if E is the potential of the half-element, $Hg|Hg_2Cl_2,xN$-HCl, and E_c is the potential of the whole cell, then

$$E = E_c + \pi + 0{\cdot}0288 + 0{\cdot}560 \text{ volt.}$$

All measurements were made at 18°, and the observed *E.M.F.* is regarded as positive if the current flows through the cell from the normal calomel electrode towards the acid solution. An inert atmosphere of nitrogen was maintained in the cells during the experiments.

Results.

The results are given in Table I. The values given under the heading E (obs.) were obtained from the above equation by using the mean of the values given under E_c.

TABLE I.

[HCl].	E_c.	π.	E (obs.).	E (calc.). (Conductivity.)	E (calc.). (Activity.)
10·09	−0·2595	0·0809	0·4102	—	0·4106
10·00	−0·2572, −0·2576, −0·2580	0·0806	0·4118	—	0·4112
7·60	−0·2121	0·0706	0·4473	—	0·4436
7·20	−0·2036, −0·2041, −0·2045	0·0674	0·4521	—	0·4494
4·64	−0·1460, −0·1462, −0·1465	0·0465	0·4891	—	0·4877
4·48	−0·1434	0·0450	0·4904	—	0·4900
2·73	−0·0970, −0·0975, −0·0975	0·0263	0·5177	—	0·5184
2·29	−0·0823	0·0205	0·5270	—	0·5263
1·00	−0·0348, −0·0348, −0·0349	0·0000	0·5540	0·5579	0·5570
0·10	+0·0590, +0·0593, +0·0595	−0·0370	0·6111	0·6137	0·6154
0·0106	+0·1528, +0·1530, +0·1531	−0·0731	0·6687	(0·6687)	(0·6687)
0·0027	+0·2121	−0·0974	0·7035	0·7032	0·7019

The potential between mercury and any solution in equilibrium with it is given by the equation:

$$E = E_0 + 0{\cdot}029 \log [Hg_2^{\cdot\cdot}] \quad . \quad . \quad . \quad . \quad (1)$$

Since the solution is saturated with respect to calomel, if the solubility product $[Hg_2^{\cdot\cdot}]\,[Cl']^2 = k_1$, then

$$E = E_0 + 0{\cdot}029 \log k_1/[Cl']^2 =$$

$$E_0 + 0{\cdot}029 \log k_1 - 0{\cdot}058 \log [Cl'] \quad . \quad . \quad (2)$$

or

$$E = E_0' - 0{\cdot}058 \log [Cl'] \quad . \quad . \quad . \quad . \quad (3)$$

The calculated values in the last two columns have been obtained from equation (3) by taking the observed value of $E = 0{\cdot}6687$ volt for $[HCl] = 0{\cdot}0106N$. In column 5, the chlorine-ion concentration has been deduced from conductivity–viscosity data for concentrations up to N-hydrochloric acid, whilst in column 6 it has been obtained from activity data (Lewis and Randall, "Thermodynamics," 1923, p. 336).

The agreement with the observed *E.M.F.* is satisfactory, but it should be pointed out that the agreement in the case of the activities cannot be regarded as an entirely independent proof, since the activity values have been derived primarily from potential measurements of cells which are virtually the same as those under consideration.

Effect of Mercuric Chloride on the Electrode Potential.—It was thought possible that mercuric chloride in presence of mercury might register a measurable potential. When such a cell was constructed from $0{\cdot}05N$-mercuric chloride in $3{\cdot}0N$-hydrochloric acid,

the usual grey film appeared on the surface of the mercury, and the *E.M.F.* measured showed wide fluctuations over several days, but tended towards the same value as the potential of the same cell containing calomel in 3·0*N*-hydrochloric acid. It was therefore concluded that the Hg–$Hg^{\cdot\cdot}$ potential is inaccessible.

The reduction of mercuric chloride by mercury is by no means rapid. Thus two solutions, each containing 13·576 g. of mercuric chloride per litre in 10*N*-hydrochloric acid, were found after 10 days' contact with mercury electrodes to contain 5·648 and 6·558 g. of mercuric chloride per litre, respectively. In more dilute solutions, the reduction is even slower; for instance, a solution of 0·05*M*-mercuric chloride in 7·6*N*-hydrochloric acid contained 12·90 and 12·32 g. of mercuric chloride per litre after 5 and 7 days' contact with mercury, respectively.

It is thus possible to have a considerable quantity of mercuric chloride in contact with mercury and calomel for a long time before equilibrium is reached, and it should therefore be possible to determine the effect of mercuric chloride on the electrode potential $2Hg–Hg_2^{\cdot\cdot}$.

Cells were constructed containing 0·05*M*-mercuric chloride, in varying concentrations of hydrochloric acid saturated with calomel, in contact with mercury. In Table II E_c' is the *E.M.F.* of the cell

TABLE II.

[HCl].	E_c'.	E_c.	[HCl].	E'.	E_c.
10·09	−0·2551	−0·2595	0·160	+0·0687	+0·0507
7·60	−0·2070	−0·2121	0·0137	+0·1625	+0·1514
5·37	−0·1565	−0·1635	0·0027	+0·2292	+0·2121
2·29	−0·0676	−0·0823			

containing 0·05*M*-mercuric chloride, and E_c that of the cell free from mercuric chloride. Both potentials represent that of the whole cell, including that of the normal calomel electrode. It will be seen that the effect of 0·05*M*-mercuric chloride on the *E.M.F.* is always small and is least in the higher concentrations of acid. The effect of mercuric chloride is to decrease the chlorine-ion concentration owing to the formation of complex ions, and from equation (2) it may be seen that this results in an increase in the *E.M.F.*

Potentials registered at an Inert Electrode.—Richards and Archibald (*Z. physikal. Chem.*, 1902, **40**, 385) have shown that a definite equilibrium exists between the components of the system

$$Hg–Hg_2Cl_2–HgCl_2,$$

provided that the three are present together; the active masses of the first two are definite but beyond analytical detection, whilst the concentration of mercuric chloride in contact with mercury and

calomel has been determined and found to be dependent on the acid concentration. If, therefore, pure mercurous chloride is brought into contact with hydrochloric acid solution, it will not be in a state of equilibrium, but will tend to decompose with separation of metallic mercury and mercuric chloride, the process going on until the equilibrium concentration of mercuric chloride is reached. At this point, as the three components are in equilibrium, the three potentials $E_{2Hg\text{-}Hg_2^{\cdot\cdot}}$, $E_{Hg_2^{\cdot\cdot}\text{-}2Hg}$, and $E_{Hg\text{-}Hg^{\cdot\cdot}}$ will be equal, hence the electrode potential between a mercury electrode and the mercurous ions measured in the above series should be equal to the oxidation potential between mercurous and mercuric ions measured at an inert platinum electrode. Measurements of this nature have been carried out. By the use of hydrochloric acid solutions of 4·6*N*, 7·2*N*, and 10·0*N*, it was found that the potentials at a platinum electrode in a solution saturated with calomel and containing concentrations of mercuric chloride less than the equilibrium concentration were identical with the electrode potentials registered above. Moreover, the mercuric chloride concentration increased until it reached the equilibrium concentration. If, however, the initial mercuric chloride concentration was greater than this, then no further increase occurred, and, moreover, the potential registered —presumably the oxidation potential—was greater than the corresponding electrode potential. Since the oxidation potential is proportional to log [$HgCl_2$], any further increase in the mercuric chloride concentration beyond the equilibrium point will result in a continuous increase in the potential. Thus it was found (compare Fig. 1, following paper) that if the potential were plotted against log [$HgCl_2$], the curve obtained was a straight line parallel to the log [$HgCl_2$] axis for low values of [$HgCl_2$], but it exhibited a definite break at the [$HgCl_2$] value corresponding to the equilibrium point, and then rose sharply.

Table III gives a comparison between the values of the equilibrium concentrations of mercuric chloride which we observed (C., L., and R.) and the values found by Richards and Archibald (R. and A.).

TABLE III.

[HCl]	4·60	5·48	7·20	7·30	10·0*N*
[$HgCl_2$] (R. and A.)	—	0·0020	—	0·0025	0·0025*M*
[$HgCl_2$] (C., L., and R.) .	0·0021	—	0·0021	—	0·0019*M*

Thus for [$HgCl_2$] values less than the equilibrium concentration the oxidation potential is less than the electrode potential and the latter is registered both at a mercury electrode and at an inert electrode. At the equilibrium point, they are equal to one another, and for higher concentrations of mercuric chloride the electrode

potential is registered at a mercury electrode and the higher oxidation potential at an inert platinum electrode.

In lower acid concentrations (0·01*N*—2·7*N*), this agreement could not be obtained. Richards and Archibald found that the equilibrium concentration of mercuric chloride in 1·0*N*- and 2·7*N*-hydrochloric acid was 0·00017*M* and 0·00076*M*, respectively. Cells constructed containing these concentrations of mercuric chloride were found to yield potentials against platinum electrodes which were, respectively, higher than the corresponding electrode potentials by 0·071 and 0·023 volt. It is probable, therefore, that in solutions which are dilute with respect to both the acid and the mercuric chloride the potential registered at the platinum electrode does not represent the true reversible oxidation potential. It was found that the same potential was registered whether the electrodes were platinised or not. Moreover, the presence of a single platinum electrode did not alter the equilibrium concentration of mercuric chloride which at 18° in *N*-hydrochloric acid was at 0·00022*M*-mercuric chloride. If, however, several electrodes (*e.g.*, four) were placed in the mixture of solution and calomel, an increase in the mercuric chloride concentration to 0·00050*M* occurred, together with the corresponding increase in potential. These phenomena are somewhat obscure and render the measurement of oxidation potentials in very dilute mercuric chloride and hydrochloric acid solutions somewhat uncertain and difficult to interpret.

Summary.

The effect of hydrochloric acid on the electrode potential between mercury and mercurous chloride in hydrochloric acid solution has been investigated over a range of acid concentration from 0·0027*N* to 10·0*N*.

Under the conditions of these experiments, the potential Hg–$Hg^{\cdot\cdot}$ was inaccessible, and the effect of mercuric chloride on the above electrode potential was small.

The equilibrium of the system Hg–Hg_2Cl_2–$HgCl_2$ has been studied in relation to the work of Richards and Archibald, and the potentials registered by this system of platinum electrodes have been described.

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CCXLVII.—*The Oxidation–Reduction Potentials of Mercurous and Mercuric Chlorides in Hydrochloric Acid Solution.*

By SYDNEY RAYMOND CARTER and ROBERT ANTHONY ROBINSON.

LITTLE attention has hitherto been devoted to the oxidation-reduction potentials of the chlorides of mercury. Although Drucker (*Z. physikal. Chem.*, 1901, **36**, 195; *Z. Elektrochem.*, 1912, **18**, 236) and Baur (*Z. physikal. Chem.*, 1908, **63**, 687) have made a few measurements in potassium chloride solution, a further investigation of the potentials in hydrochloric acid solution is desirable in view of the complicated behaviour of mercury halides in the presence of halogen acids, and also of the recent investigations of Stewart and Wardlaw (J., 1922, **121**, 1481) on the action of sulphur dioxide on these two chlorides which can be correlated with the electrochemical properties of these systems.

EXPERIMENTAL.

Preliminary experiments indicated that it would be a matter of considerable difficulty to obtain steady reproducible potentials corresponding with the oxidation process $Hg_2^{\cdot\cdot} \longrightarrow 2Hg^{\cdot\cdot}$. In the first place, it was found that a 0·1*M*-solution of mercuric chloride saturated with calomel and containing no acid had so low a conductivity that potential measurements were impossible. Secondly, in solutions of 0·1*N*-hydrochloric acid saturated with calomel and containing mercuric chloride, it was found that no agreement could be obtained between the potentials registered at platinised platinum electrodes; moreover, the potential varied widely with time. In a similar solution containing 0·0005*M*-mercuric chloride, a large fall in potential was observed over several days, but after this a reading was obtained which was fairly constant and almost equal to the electrode potential of mercury and calomel in 0·1*N*-hydrochloric acid. Since the electrodes had become covered with a grey deposit of mercury, it was concluded that an electrode and not an oxidation potential was being measured.

A number of similar experiments were performed with the same result. Shaking the calomel with the solution of hydrochloric acid and mercuric chloride for 12 hours did not give a more constant potential reading. It was noticed, however, that if the electrodes were completely buried to a considerable depth in a paste of calomel instead of being suspended in the solution, and if the dissolved air in the solution were removed by means of a current of purified nitrogen, it was possible to obtain potentials which gave good

agreement between different electrodes over considerable periods of time and were reproducible. Moreover, they were distinct from the electrode potentials described in the preceding paper. The necessity for the complete immersion of the electrodes is probably due to the low concentration of mercurous ions, the passage of a very small current in the course of potential measurements being sufficient to exhaust the supply of mercurous ions in the vicinity of the electrode if this is simply suspended in the solution. Complete immersion of the electrode in the paste ensures full saturation in its vicinity.

Cells of the following type were constructed :

$$\mathrm{Pt}\left|\begin{matrix}\mathrm{Hg_2Cl_2}\\ x\mathit{M}\text{-}\mathrm{HgCl_2}\\ y\mathit{N}\text{-HCl}\end{matrix}\right|y\mathit{N}\text{-HCl}\left|\mathit{N}\text{-HCl}\right|\mathit{N}\text{-KCl}\left|\mathit{N}\text{-KCl},\mathrm{Hg_2Cl_2}\right|\mathrm{Hg}.$$

The chain of intermediate solutions has been shown to be sufficient to maintain constant reproducible diffusion junctions (Carter and Lea, J., 1925, **127**, 487; Carter, Lea, and Robinson, preceding paper), and possesses the advantage that the potential at each junction can be determined with the necessary degree of accuracy. The system differs from the previously investigated systems of iron and copper salts (Carter and Clews, J., 1924, **125**, 1880; Carter and Lea, J., 1925, **127**, 499) in that only the mercuric chloride and the hydrochloric acid concentrations in the oxidation cell can be subjected to variation, since the calomel cannot be varied in concentration owing to its low solubility. It is essential, however, to maintain the solution saturated with respect to the calomel in order to obtain a defined system.

The oxidation cell consisted of a glass vessel containing a solution of mercuric chloride and hydrochloric acid in the requisite proportion and saturated with respect to calomel. Experiments showed that platinisation of the electrodes did not increase their sensitivity, nor was the shape or form of the electrodes a factor influencing the potential readings. Three electrodes of polished platinum foil (about 1 sq. cm. in area) were actually employed.

Measurements of each of the cells were carried out, in general, over a period of a week, a lapse of 12—24 hours after construction being necessary before a constant potential was registered. Renewal of the liquid boundaries during this period showed that no appreciable change had occurred in the diffusion potentials. All potentials are referred to the absolute scale. A positive sign indicates that the current flows through the cell from the calomel electrode to the oxidation element. All measurements were made at 18°. Concentrations of mercuric chloride are given as g.-mols. per litre.

Potential Measurements.—If E is the potential of the oxidation element, π the diffusion potential between xN- and N-hydrochloric acid (Carter and Lea, *loc. cit.*), 0·0288 volt the diffusion potential between N-hydrochloric acid and N-potassium chloride (calculated on the basis of Henderson's formula, *Z. physikal. Chem.*, 1907, **59**, 118), and E_c the potential of the whole cell, then:

$$E = E_c + \pi + 0{\cdot}0288 + 0{\cdot}560 \text{ volt.}$$

The values for one experiment given in Table I are typical of the degree of accuracy attained.

TABLE I.

Cell made up as: $[HCl] = 1{\cdot}00N$, $[HgCl_2] = 0{\cdot}75M$.
Final composition by analysis: $[HCl] = 0{\cdot}96N$, $[HgCl_2] = 0{\cdot}735M$.

Time (days).	0.	1.	2.	3.	4.	5.
Electrode No. 1	(0·2654)	0·3026	0·2974	0·3012	0·2988	0·3006
„ „ 2	(0·2644)	0·3026	0·2966	0·3006	0·2988	0·3006
„ „ 3	(0·2634)	0·3026	0·2970	0·3012	0·2988	0·3006

Average potential (neglecting readings on first day) = 0·3000 volt.
Average error = ±0·0017 volt.

In Table II are given the potentials of a number of cells, showing the effect of varying the mercuric chloride concentration in solutions of hydrochloric acid of the following concentrations: 0·01, 0·1, 0·5, 1·0, 2·7, 4·6, 7·2, and 10·0N.

TABLE II.

Cell No.	[HCl].	[$HgCl_2$].	E_c.	π.	E.
		$[HCl] = 0{\cdot}01N$.			
1	0·0100	0·00013	0·2810	−0·0740	0·7958
2	0·0100	0·00119	0·3258	−0·0740	0·8406
3	0·0100	0·0154	0·3868	−0·0740	0·9016
4	0·0104	0·100	0·4671	−0·0734	0·9825
5	0·0100	0·150	0·4897	−0·0740	1·0045
		$[HCl] = 0{\cdot}10N$.			
6	0·0995	0·000256	0·1972	−0·0370	0·7490
7	0·100	0·0018	0·2385	−0·0370	0·7903
8	0·099	0·0103	0·2719	−0·0370	0·8237
9	0·106	0·0199	0·2912	−0·0360	0·8440
10	0·100	0·100	0·3603	−0·0370	0·9121
11	0·096	0·134	0·3735	−0·0375	0·9248
12	0·100	0·213	0·4082	−0·0370	0·9600
		$[HCl] = 0{\cdot}5N$.			
13	0·509	0·00057	0·1119	−0·0106	0·6901
14	0·508	0·00193	0·1347	−0·0106	0·7129
15	0·507	0·020	0·1842	−0·0106	0·7624
16	0·500	0·196	0·2750	−0·0106	0·8532
17	0·500	0·470	0·3329	−0·0106	0·9111

TABLE II (*contd.*).

[HCl] = 1·0*N*.

Cell No.	[HCl].	[$HgCl_2$].	E_c.	π.	E.
18	1·005	0·00053	0·0272	0	0·6160
19*	1·000	0·00099	0·0433	0	0·6321
20	1·050	0·00198	0·0564	+0·0008	0·6460
21	0·964	0·0196	0·1051	−0·0007	0·6932
22	0·960	0·0208	0·1080	−0·0008	0·6960
23	0·980	0·072	0·1543	−0·0004	0·7427
24	0·995	0·096	0·1616	0	0·7504
25	0·991	0·169	0·1911	0	0·7799
26	0·960	0·735	0·3000	−0·0008	0·8880
27	0·920	0·985	0·3207	−0·0014	0·9081
28	1·000	1·010	0·3292	0	0·9180

* Cell No. 19 contained four electrodes, two of polished platinum foil and two of platinised platinum foil. They all gave identical results.

[HCl] = 2·7*N*.

29	2·73	0·0004	−0·0885	0·0257	0·5260
30	2·74	0·0024	−0·0526	0·0258	0·5620
31	2·74	0·0052	−0·0330	0·0258	0·5816
32	2·72	0·020	−0·0032	0·0256	0·6112
33	2·72	0·051	+0·0253	0·0256	0·6397
34	2·72	0·100	+0·0409	0·0256	0·6553
35	2·70	0·407	+0·1043	0·0250	0·7181
36	2·61	0·910	+0·1641	0·0240	0·7769
37	2·72	2·260	+0·2376	0·0256	0·8520

[HCl] = 4·6*N*.

38	4·68	0·0026	−0·1422	0·0469	0·4935
39	4·66	0·0032	−0·1355	0·0468	0·5001
40	4·67	0·021	−0·0825	0·0467	0·5530
41	4·62	0·024	−0·0791	0·0465	0·5562
42	4·53	0·192	−0·0160	0·0457	0·6185
43	4·63	0·529	+0·0238	0·0466	0·6592
44	4·44	0·966	+0·0480	0·0450	0·6818
45	4·60	1·033	+0·0543	0·0463	0·6894
46	4·60	3·80	+0·1494	0·0463	0·7845

[HCl] = 7·2*N*.

47	7·40	0·0028	−0·1994	0·0667	0·4561
48	7·30	0·0108	−0·1674	0·0680	0·4894
49	7·18	0·0961	−0·1082	0·0673	0·5479
50	7·40	0·977	−0·0322	0·0685	0·6251
51	7·20	3·80	+0·0318	0·0674	0·6880

[HCl] = 10·0*N*.

52	10·05	0·0039	−0·2374	0·0808	0·4322
53	10·19	0·0117	−0·2104	0·0815	0·4599
54	10·19	0·0986	−0·1518	0·0815	0·5185
55	10·05	0·937	−0·0836	0·0808	0·5860
56	10·00	3·80	−0·0314	0·0806	0·6380

Variation of Potential with Concentration of Mercuric Chloride.—In Fig. 1 the potential of the oxidation element is plotted against the

logarithm of the mercuric chloride concentration, for each acid concentration. According to the equation:

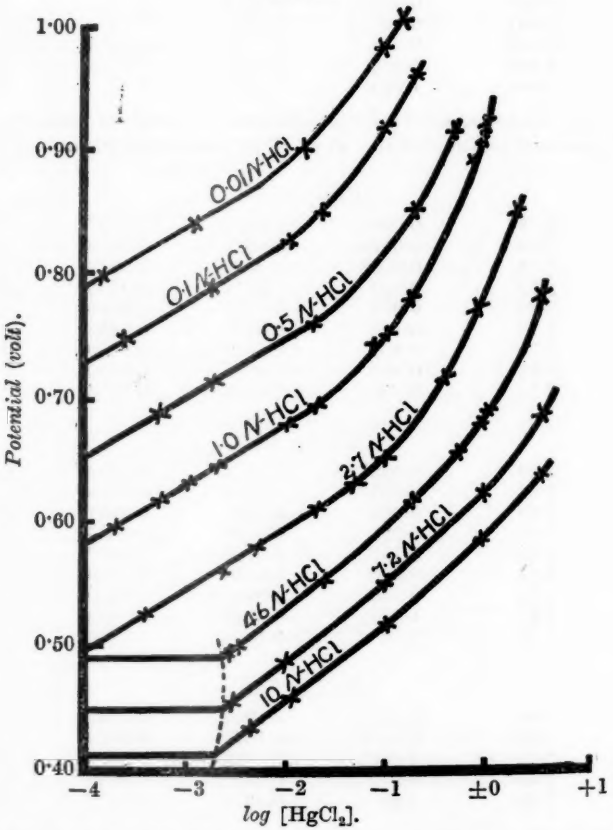
$$E = E_0 + 0{\cdot}029 \log [Hg^{\cdot\cdot}]^2/[Hg_2^{\cdot\cdot}] \quad . \quad . \quad . \quad (1)$$

since $$[Hg^{\cdot\cdot}] = k_2[HgCl_2]/[Cl']^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and $$[Hg_2^{\cdot\cdot}] = k_1/[Cl']^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

therefore $$E = E_0 + 0{\cdot}029 \log k_2{}^2[HgCl_2]^2/k_1[Cl']^2 \quad . \quad . \quad (4)$$

FIG. 1.



It follows that for a given acid concentration, the mercurous-ion concentration is constant, whilst the mercuric-ion concentration will be proportional to $[HgCl_2]$ since the feeble ionisation of mercuric chloride renders its contribution to the chlorine-ion concentration negligible.

Hence $$E = E_0' + 0{\cdot}058 \log [HgCl_2] \quad . \quad . \quad . \quad . \quad (5)$$

or the *E.M.F.* is a linear function of the logarithm of the mercuric chloride concentration.

From the graph, it will be seen that the logarithmic law holds in the more dilute solutions of mercuric chloride, but breaks down when the concentrations of mercuric chloride and hydrochloric acid are of the same order. It is noteworthy that in place of the theoretical slope of 0·058 volt for a ten-fold dilution, we obtained slopes of 0·060 volt in the 4·6*N*-, 7·2*N*-, and 10·0*N*-hydrochloric acid solutions, and of 0·047 volt in the lower acid concentrations. The discrepancy in the former case is not serious, but in the latter case is beyond the range of experimental error, and up to the present we have not been able to account for it.

To explain the deviations from the logarithmic law in the more concentrated mercuric chloride solutions, complex-ion formation may be assumed. Complex-ion formation between calomel and hydrochloric acid is unlikely, as calomel is known to form only a few double salts. Sherrill (*Z. physikal. Chem.*, 1903, **43**, 705; 1904, **47**, 103) and Noyes and Le Blanc (*Z. physikal. Chem.*, 1890, **6**, 389) have brought forward evidence in favour of the existence of the ion $HgCl_4''$, whilst Sand and Breest (*Z. physikal. Chem.*, 1907, **59**, 424) and Drucker (*Z. Elektrochem.*, 1912, **18**, 236) consider that the ion has the formula $HgCl_3'$. As the percentage of mercuric chloride in the form of complex ions is high, it may be seen from the equations $HgCl_2 + 2Cl' = HgCl_4''$ and $HgCl_2 + Cl' = HgCl_3'$ that when the mercuric chloride is present in the same concentration as the acid, a considerable decrease in the acid concentration must occur in order to allow the formation of these complex ions, and hence, according to equation (4), the potential of the cell will be increased. Quantitatively the behaviour of the system is given by equation (4) and an equation determining the equilibrium of the complex ion. According to Sherrill,

$$[HgCl_4'']/[HgCl_2][Cl']^2 = 70 \quad . \quad . \quad . \quad . \quad (6)$$

whilst according to Sand and Breest (if the value of the constant as recalculated by Drucker be used),

$$[HgCl_3']/[HgCl_2][Cl'] = 11{\cdot}5 \quad . \quad . \quad . \quad . \quad (7)$$

These two views have been reconciled by Linhart (*J. Amer. Chem. Soc.*, 1915, **37**, 258; 1916, **38**, 1272) who considers that both the ions $HgCl_3'$ and $HgCl_4''$ are present in solution [together with small quantities of polymerised mercuric chloride, $(HgCl_2)_2$, and the complex ions Hg_2Cl_5 and Hg_2Cl_6''], the equilibrium conditions being given by the equations:

$$[HgCl_3']/[HgCl_2][Cl'] = 9{\cdot}8 \quad . \quad . \quad . \quad . \quad (8)$$

$$[HgCl_4'']/[HgCl_3'][Cl'] = 4{\cdot}9 \quad . \quad . \quad . \quad . \quad (9)$$

and therefore $$[HgCl_4'']/[HgCl_2][Cl']^2 = 48 \quad . \quad . \quad . \quad . \quad (10)$$

From equation (9) it follows that in N-hydrochloric acid solution the complex ion $HgCl_4''$ is predominant, but in 0·01 N-acid solution the $HgCl_3'$ ion is the main constituent, whilst in 0·1N- and 0·5N-acid both ions are present in comparable amounts. We may therefore, as an approximation, apply equation (10) to solutions of mercuric chloride in N-hydrochloric acid. It is difficult to solve this equation to give the amounts of free unbound mercuric chloride in equilibrium with free acid and complex ion, but it is easy to proceed in the reverse manner. Thus, for any given total acid concentration [HCl], if an arbitrary value of the concentration of complex ion $[HgCl_4'']$ be assumed, it follows that the concentration of the free acid is $\{[HCl]–2[HgCl_4'']\}$, and hence the concentration of chlorine ion is $\{[HCl]–2[HgCl_4'']\}\gamma$, where γ is the activity coefficient corresponding with the concentration of the free hydrochloric acid. Hence by substitution in equation (6) we can determine the concentration of free mercuric chloride. The sum of free and combined mercuric chloride gives the total concentration of mercuric chloride, since that of the $Hg^{\cdot\cdot}$ and $HgCl^{\cdot}$ ions is negligible. The concentrations of free mercuric chloride and of chlorine ions may now be substituted in equation (4), together with the values of the constants $E = 1{\cdot}190$ volt, $k_1 = 3{\cdot}5 \times 10^{-18}$, and $k_2 = 10^{-14}$, to give a calculated value of the $E.M.F.$ corresponding with given values of [HCl] and total mercuric chloride.

Hence we obtain Table III, which gives the calculated values of the potential corresponding to different total concentrations of mercuric chloride in N-hydrochloric acid on the assumption that $HgCl_4''$ ions are formed.

TABLE III.

$[HCl] = 1{\cdot}0N.$

$[HgCl_4'']$.	Free [HCl].	γ.	$[Cl']$.	Free $[HgCl_2]$.	Total $[HgCl_2]$.	E (calc.).	E (obs.).
0·40	0·2	0·783	0·157	0·338	0·738	0·903	0·883
0·30	0·4	0·763	0·305	0·0672	0·367	0·846	0·825
0·10	0·8	0·796	0·637	0·00513	0·105	0·763	0·752
0·05	0·9	0·811	0·730	0·00195	0·0520	0·735	0·722
0·01	0·98	0·821	0·805	0·000322	0·0103	0·687	0·680

It will be seen that the considerable deviations from the logarithmic law that occur in concentrated solutions of mercuric chloride can be accounted for by assuming the existence of the ion $HgCl_4''$. If it is borne in mind that the values of k_1 and k_2 given above are strictly applicable only at 25° and not at 18°, that there are polymerised molecules $(HgCl_2)_2$, which give rise to Hg_2Cl_5' and Hg_2Cl_6'' ions, also present in solution, and moreover, that the formation of the complex ion $HgCl_4''$ causes a considerable reduction in the chlorine-ion concentration in the more concentrated mercuric chloride solutions,

which in turn favours the formation of $HgCl_3'$ ions, it will be seen that the method can only be expected to yield an approximation to the observed values of the potentials. However, the agreement is sufficient to show that the observed potentials can be accounted for on the basis of complex-ion formation.

Since in 0·1*N*- and 0·5*N*-hydrochloric acid both $HgCl_3'$ and $HgCl_4''$ ions are present to about the same extent, it is difficult to calculate the distribution of mercuric chloride between the various complex ions and to obtain calculated values of the potentials in these dilute acid solutions.

In the case of the three highest concentrations of acid, the portions of the curves parallel to the log $[HgCl_2]$ axis represent the potentials registered in solutions in which the mercuric chloride concentration is not high enough for equilibrium between $Hg–Hg_2Cl_2–HgCl_2$ to obtain. Under these conditions it was found that an oxidation potential was not registered, since it was independent of the mercuric chloride concentration, but a potential identical with the electrode potential of mercury and calomel described in the previous paper, and the data for the latter were used for plotting the horizontal portions of the curves. Such systems were found to be unstable since mercurous chloride decomposed into mercury and mercuric chloride until the concentration of the latter corresponded with the equilibrium value for the acid concentration under consideration.

Variation of Potential with Acid Concentration.—By drawing a line perpendicular to the abscissa and cutting it at the desired value of the mercuric chloride concentrations, we have read off from the curves in Fig. 1 the values of the potential of a cell in which the mercuric chloride concentration is constant and the hydrochloric acid concentration is varied between 0·01*N* and 10*N*. This has been done for five values of the former, namely, 1·0, 0·1, 0·01, 0·001, and 0·0001*N*. The results are in Table IV.

TABLE IV.

	$[HgCl_2]$, *M*.					
[HCl].	0·0001	0·001	0·01	0·1	1·0	4·0.
	Potential (volt).					
0·01	0·7910	0·8375	0·8885	0·9820	—	—
0·10	0·7295	0·7775	0·8260	0·9130	—	—
0·5	0·6530	0·7005	0·7475	0·8155	—	—
1·0	0·5840	0·6325	0·6795	0·7500	0·9110	—
2·7	0·4960	0·5455	0·5960	0·6550	0·7850	—
4·6	—	—	0·5305	0·5945	0·6860	0·7960
7·2	—	—	0·4890	0·5500	0·6240	0·6925
10·0	—	—	0·4560	0·5180	0·5875	0·6400

These results have been plotted in Fig. 2, which shows the relation between potential and hydrochloric acid concentration. This graph

also contains the curve of the electrode potential $2Hg–Hg_2^{\cdot\cdot}$ against acid concentration, based upon data given in the preceding paper.

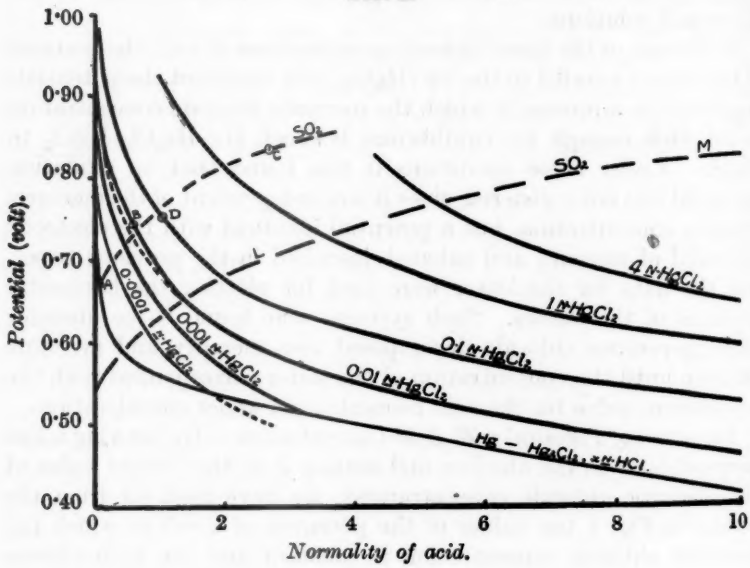
On the assumption that the ions $HgCl_3'$ and $HgCl_4''$ are formed according to equations (8) and (10), and since

$$[HgCl_4''] + [HgCl_3'] + [HgCl_2] = [HgCl_2]_{total}$$

then $$[HgCl_2]_{total} = [HgCl_2]\{1 + 9{\cdot}8[Cl'] + 48[Cl']^2\}$$

or $$[HgCl_2] = [HgCl_2]_{total}/\{1 + 9{\cdot}8[Cl'] + 48[Cl']^2\}.$$

FIG. 2.



Hence from equation (4)

$$E = E_0 + 0{\cdot}029 \log k_2^2/k_1 + 0{\cdot}058 \log [HgCl_2]_{total} / [Cl']\{1 + 9{\cdot}8[Cl'] + 48[Cl']^2\}$$

or $$E = E_0 + 0{\cdot}029 \log k_2^2/k_1 + 0{\cdot}058 \log [HgCl_2]_{total} - 0{\cdot}058 \log [Cl']\{1 + 9{\cdot}8[Cl'] + 48[Cl']^2\}.$$

In 0·01*M*-mercuric chloride, as the concentration of this salt is so low that the formation of these complex ions does not affect the concentration of acid appreciably, then for a constant value of $[HgCl_2]_{total}$ values of E corresponding to different concentrations of hydrochloric acid may be calculated.

In Fig. 2, the dotted curve indicates the potentials calculated in this manner, compared with the observed potentials, which are indicated by a continuous line. It is evident that good agreement has been obtained for concentrations of hydrochloric acid between 0·01*N* and 1·0*N*; for higher concentrations, however, the calculated

potentials decrease much more rapidly than the observed. It is difficult to account for this behaviour, partly because the activities of the different complex ions may vary in an unknown manner in concentrated acid solution, partly because the actual nature of these ions is unknown, and partly because the complex acids may not be completely dissociated. It may be pointed out, however, that in the most concentrated acid solutions the oxidation potential varies in the same way as the $Hg|Hg_2Cl_2,xN$-HCl potential, *i.e.*, it is proportional to $-0{\cdot}058 \log [Cl']$, the chlorine-ion concentration being calculated on the basis of activity data. This indicates that the system is behaving as if complex-ion formation ceased in the high acid concentrations and as if it conformed to its normal behaviour according to equation (4). Although there is no theoretical reason for this supposition, it is interesting to notice that Richards and Archibald (*Z. physikal. Chem.*, 1902, **40**, 385; compare preceding paper) found that the amount of mercuric chloride in equilibrium with mercury and calomel was independent of the acid concentration provided this was above $5N$. As almost all the mercuric chloride is present as complex ion, this is equivalent to saying that above $5N$-hydrochloric acid complex-ion formation is not increased by increasing the acid concentration.

The Action of Sulphur Dioxide on the Chlorides of Mercury.—In Fig. 2, we have indicated the variation of the oxidation–reduction potential of sulphur dioxide by the curve LM (Carter and James, J., 1924, **125**, 2234). Stewart and Wardlaw (*loc. cit.*) have studied the action of sulphur dioxide on the two chlorides of mercury, and in considering their results we have been guided by the principle that the system possessing the higher potential will oxidise the other system, being itself reduced.

The various reactions between mercury salts, hydrochloric acid, and sulphur dioxide were found to be extremely sensitive to small changes in acid concentration, and this is in agreement with the steepness of the potential curves, particularly in the region of low acid concentration.

(a) *Action of sulphur dioxide on calomel.* At 95°, Stewart and Wardlaw found that sulphur dioxide acted on calomel suspended in hydrochloric acid, in four ways, depending on the concentration of acid:

(1) $8N$- to $2N$-acid. Oxidation of calomel to mercuric chloride occurs, being complete only in the most concentrated acid and slight in $2N$-acid.

(2) $2N$- to $0{\cdot}16N$-acid. Decomposition of calomel and darkening of the solution, according to the equation: $Hg_2Cl_2 \longrightarrow Hg + HgCl_2$. We have confirmed the fact that this reaction is independent of the

sulphur dioxide; moreover, it ceases at approximately 0·16*N*-acid, because calomel could be boiled for several hours in 0·10*N*-acid without the slightest darkening.

(3) 0·16*N*- to 0·07*N*-acid. Inert region—calomel unaffected.

(4) 0·02*N*- to zero acid. Calomel is reduced to mercury by sulphur dioxide.

According to our graph, for acid concentrations between zero and 0·2*N*, the sulphur dioxide potential is lower than the $Hg–Hg_2Cl_2$ potential and hence reduction of the calomel is to be expected corresponding to (4).

Between 0·2*N*- and *N*-hydrochloric acid, it is to be expected that the oxidising action of sulphur dioxide on calomel will be slight, because the amount of mercuric chloride that must be formed to raise the oxidation potential as high as the sulphur dioxide potential is very small. Observation in this region is hindered by the fact that simultaneous decomposition of the calomel occurs into mercury and mercuric chloride. Above 2*N*-acid the oxidation of calomel becomes considerable and, according to our graph, should proceed almost to completion. It seems probable that equilibrium was not attained in all the experiments of Stewart and Wardlaw.

The point A on Fig. 2 represents the point on the $Hg–Hg_2Cl_2$ electrode potential curve (at 0·02*N*-HCl) where it intersects the sulphur dioxide curve.

(b) *Action of sulphur dioxide on mercuric chloride.* Stewart and Wardlaw found that if sulphur dioxide was passed for 12 hours through a solution of mercuric chloride in 0·48*N*-hydrochloric acid at 95°, calomel was formed, the amount decreasing with lowering of the mercuric chloride concentration, so that when $[HgCl_2] = 0{\cdot}0094M$ the amount of calomel formed by reduction was very small. It therefore follows that the oxidation potential of sulphur dioxide in acid of this concentration is less than the oxidation of the mercury system when $[HgCl_2]$ is greater than 0·0094*M*, and greater than the oxidation potential when $[HgCl_2]$ is less than 0·0094*M*. This gives the point B in Fig. 2.

In 2·64*N*-hydrochloric acid, Stewart and Wardlaw found that mercuric chloride was not reduced until its concentration reached 1·92*M*. This gives the point C. In 1·0*N*-acid, the extent of reduction was very small when $[HgCl_2] = 0{\cdot}1M$. This is the point D.

It will be seen that the line AC drawn through these four points gives a curve for the oxidation potential of sulphur dioxide which is similar in form to the curve LM based on direct potential measurements, but it is displaced upwards by about 0·2 volt. The discrepancy may be partly attributed to the different temperatures at

which our experiments and those of Stewart and Wardlaw were carried out, *viz.*, 18° and 95°, respectively.

Summary.

The conditions necessary for obtaining reproducible oxidation potentials of mercurous and mercuric chlorides in hydrochloric acid solution at 18° have been examined. The influence on potential of various concentrations of both the mercuric chloride and the hydrochloric acid has been determined over a wide range.

The departures from the logarithmic law that have been observed have been attributed to a large extent to the formation of complex ions.

Evidence has been adduced in favour of the existence of complex ions, especially $HgCl_4''$, in hydrochloric acid solutions of mercuric chloride.

The abnormal effect of hydrochloric acid stronger than 5*N* on the complex-ion formation, noticed by Richards and Archibald, has been confirmed.

The reactions of sulphur dioxide on the chlorides of mercury have been studied in the light of the electrochemistry of these systems.

The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research for a grant to one of them (R. A. R.) which has enabled this research to be carried out.

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CCXLVIII.—*The Decomposition of Nitrous Acid in Aqueous Solution.*

By THOMAS WESTON JOHNS TAYLOR, ERNEST WILLIAM WIGNALL, and JOHN FREDERICK COWLEY.

THE decomposition of nitrous acid in aqueous solution is a complex phenomenon. The more important facts already known can be summarised as follows: (1) In contact with air, there is a certain amount of oxidation; if an inert gas replaces air, the reaction $3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$ takes place (Montemartini, *Atti R. Accad. Lincei*, Rendiconti, 1890, **6**, ii, 263). (2) The rate of decomposition follows approximately a unimolecular law, in contact either with air (Ray, Dey, and Ghosh, J., 1917, **111**, 413) or with carbon dioxide (Montemartini, *loc. cit.*). (3) The rate is reduced by adding nitric oxide to the gas above the solution, and is slower

the greater the pressure of nitric oxide (Montemartini, *loc. cit.*; Klemenc and Pollak, *Z. physikal. Chem.*, 1922, **101**, 150). (4) The rate is much increased by bubbling an inert gas through the solution (Knox and Reid, *J. Soc. Chem. Ind.*, 1919, **38**, 105T) and apparently reaches no limit as the speed of bubbling is increased (Klemenc and Pollak, *loc. cit.*). (5) The reaction is reversible (Veley, *Chem. News*, 1892, **66**, 175), but the reverse reaction proceeds extremely slowly with dilute solutions of nitric acid (Saposhnikov, *J. Russ. Phys. Chem. Soc.*, 1900, **32**, 375; 1901, **33**, 306).

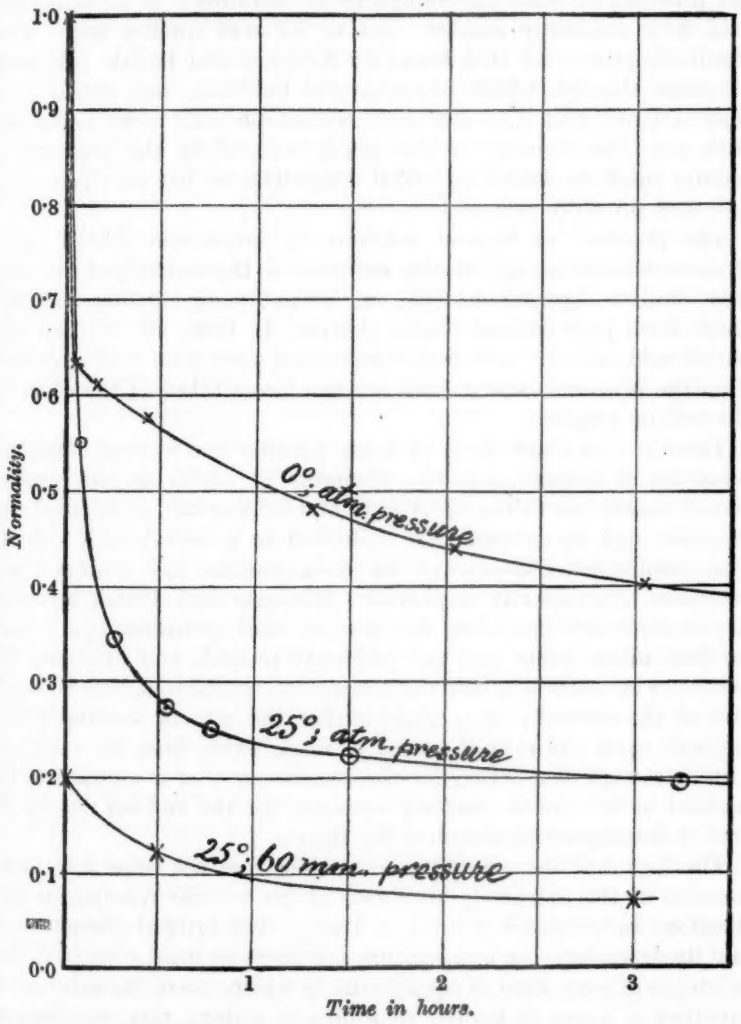
In an attempt to find conditions under which solutions of nitrous acid would be sufficiently stable for investigation of its reactions, the effect of reducing the area of surface of the solution in contact with the gas phase was tried. This can be done most simply by floating a layer of an immiscible liquid on the top of the solution; most liquids which might be used, however, such as benzene or ligroin, dissolve nitrogen trioxide from fairly strong solutions of nitrous acid, but the solubility of the trioxide is smaller in the mixture of higher paraffins sold as "medicinal paraffin," and this liquid has the added advantage that its high viscosity makes it possible to stir the lower aqueous layer without breaking up the paraffin layer.

Dilute solutions of nitrous acid prepared beneath a layer of this paraffin from a solution of pure barium nitrite (Witt and Ludwig, *Ber.*, 1903, **36**, 4384) and the equivalent of dilute sulphuric acid, and thus containing barium sulphate in suspension, are considerably more stable than similar solutions under nitrogen and very much more stable than those in contact with air. For example, equal volumes of a solution in identical vessels were kept at 25°, the one under paraffin and the other in contact with air; after 3 hours, the first showed 5% decomposition and the second 53%. Quite dilute solutions, *i.e.*, 0·1*N* and less, could be kept at 0° for 5 hours without the decomposition exceeding 4%. The solutions were stirred during these experiments by a small stirrer passing through the paraffin, but not at such a rate as to draw gas bubbles into the solution; the concentration of acid was determined by Veley's method (*Proc. Roy. Soc.*, 1893, *A*, **52**, 28).

When stronger solutions were investigated under paraffin, it was found that critical concentrations existed above which the rate of decomposition was very rapid and below which it was much slower. The critical concentration depends on the temperature, being higher the lower the temperature, and on the pressure of air above the paraffin, increasing with the pressure. Fig. 1 shows the rate of decomposition in two solutions, originally of *N* concentration, at 25° and at 0°, and also the effect at 25° of reducing to 60 mm. the pressure above a 0·2*N*-solution, *i.e.*, one which at atmospheric

pressure would decompose but slowly. Ray, Dey, and Ghosh (*loc. cit.*) noted this critical phenomenon and could not obtain a solution stronger than 0·185*N* which did not evolve nitric oxide rapidly when at 0° and in contact with air.

FIG. 1.



The velocity of the "slow" reaction at 25° was measured, and the results of any one experiment roughly agreed with the unimolecular law, although the velocity coefficient slowly decreased as the reaction proceeded; but the reaction is in no sense truly uni-

molecular—even well below the critical concentration the value of the velocity coefficient depends on the initial concentration and on the shape of the vessel in which the solution is kept, and thus has no absolute significance.

The velocity of the reaction under paraffin is also influenced by the presence of other substances in the solution; in 5*N*-sulphuric acid it is markedly smaller, and in 7*N*-acid smaller still. This result disagrees with that found by Klemenc and Pollak, who used solutions through which nitrogen was bubbling, but agrees with that of Knox and Reid (*loc. cit.*), whose solutions were in contact with air. The velocity is also much reduced by the presence of sodium sulphate, which at 0·65*M* concentration has an effect equivalent to 5*N*-sulphuric acid.

The presence of barium sulphate in suspension during these experiments had no appreciable influence on the stability of the acid, since similar experiments were carried out using nitrous acid prepared from pure sodium nitrite (Divers, J., 1899, **75**, 80) and sulphuric acid, and the rates of decomposition were those to be expected from the previous experiments, account being taken of the effect of the sodium sulphate.

These results show that, by using paraffin and sodium sulphate, solutions of nitrous acid the strengths of which do not exceed certain maximum values (0·4*N* at 0° and 0·2*N* at 25°, at atmospheric pressure) can be conveniently stabilised to a considerable extent. The complicated character of the decomposition has, however, not yet been satisfactorily explained. Klemenc and Pollak advance the improbable hypothesis that nitrous acid spontaneously breaks up into nitric oxide and the hydroxyl radical, and attribute its existence in solution to mutual action between molecules of the acid and of the solvent; they suggest that the rate of decomposition depends upon the rate of escape of nitric oxide from the solution. This, although accounting for the sensitiveness of a solution to its method of treatment, scarcely accounts for the sudden change in rate of decomposition shown in the figure.

The fact that the reaction is reversible does not come into play, because of the extremely slow rate of the reverse reaction at the dilutions investigated [see (5), p. 1924]. The critical phenomenon and its dependence on temperature and pressure must arise from the existence of some kind of equilibrium in which one of the substances involved is a gas of limited solubility in water; this equilibrium must be established with great rapidity to account for the observations of Klemenc and Pollak [(4), p. 1924].

The view advanced here is that in a solution of nitrous acid the equilibrium $2HNO_2 \rightleftharpoons N_2O_3 + H_2O$ is set up, and that the com-

plicated nature of the decomposition arises from the behaviour of the anhydride; that this latter exists in solution is supported by the observations of Saposhnikov (*loc. cit.*) on the ease with which organic solvents will dissolve it from solutions of the acid. It is not the anhydride itself which escapes as gas from the solution, for, if this were so, the solution would contain eventually less nitric acid than the quantity corresponding to the equation of decomposition [(1), p. 1923], and experiment showed that in every case under paraffin the theoretical amount of nitric acid remained. If, however, the further equilibrium $N_2O_3 \rightleftharpoons NO + NO_2$ tends to be set up in solution, the facts receive an intelligible explanation. In a completely stable solution, the concentration of water being assumed to be constant, the function $[NO][NO_2]/[HNO_2]^2$ would have a fixed value at any one temperature; but the concentration of nitric oxide cannot exceed a certain limit because of its slight solubility, and the limit will depend on the pressure. The existence of the "rapid" decomposition is accounted for. No completely stable solution, however, can exist, even in a sealed bulb where the pressure of nitric oxide can become high (Montemartini, *loc. cit.*), since the nitrogen peroxide is continually hydrated and removed from the equilibrium. During the "slow" decomposition two factors come into play: the rate of escape of nitric oxide and the rate of hydration of the peroxide. The concentration of the latter is probably extremely small and thus the quantity hydrated in unit time is small, and consequently the second factor under normal conditions is of less importance. Any factor tending to facilitate the escape of the nitric oxide, such as increased area of contact with the gas phase, addition of sand or charcoal (Frémy, *Compt. rend.*, 1870, **70**, 63), or reduction of pressure, will increase the rate of decomposition. The escape of a gas from solution has a rapid stage, followed by a slower stage (Perman, J., 1895, **67**, 868; Bohr, *Ann. Physik*, 1899, **68**, 507; Findlay and King, J., 1913, **103**, 1170) which follows a logarithmic law, thus agreeing with the behaviour of nitrous acid. The effect of added substances in reducing the rate of decomposition can be compared with the result found by Bohr that carbon dioxide escapes less rapidly from a solution of sodium chloride than from pure water.

Work is in progress on various reactions of nitrous acid stabilised in the manner described in this paper.

Our thanks are due to Dr. W. H. Mills for his helpful criticism and to Messrs. Brunner Mond & Co., Ltd., for their generosity in making a grant which has covered part of the expenses of this work.

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CCXLIX.—*The Action of the Metallic Derivatives of Ethyl Dehydroundecenoate upon Alkyl Halides.*

By WILLIAM WHALLEY MYDDLETON and RUDOLPH G. BERCHEM.

AN attempt to synthesise Δ^{10}-stearolic acid by acting upon the silver derivative of ethyl dehydroundecenoate with heptyl bromide in alcoholic solution resulted in the formation of silver bromide, ethyl heptyl ether, and free ethyl dehydroundecenoate. With the silver derivative in absence of alcohol, an excess of heptyl bromide gave silver bromide, heptene, and ethyl dehydroundecenoate. In each case, the yields of silver bromide and ethyl ester were practically quantitative.

n-Propyl, *iso*butyl and ethyl bromides and ethyl iodide were used in succession, and in each case quantitative yields of silver halide and ethyl dehydroundecenoate were obtained. Other products in these reactions were not investigated. The silver derivative obviously reacts with halogen acid derived from the alkyl halide.

During the preparation of the silver derivative by the action of alcoholic silver nitrate upon the ester, we followed the reaction more closely than Krafft (*Ber.*, 1896, **29**, 2232) and found the yields of silver derivative and free nitric acid required for the equation:

$$CH{:}C{\cdot}[CH_2]_8{\cdot}CO_2Et + 2AgNO_3 = AgNO_3,CAg{:}C{\cdot}[CH_2]_8{\cdot}CO_2Et + HNO_3.$$

We add to Krafft's observations that the silver derivative is soluble in hot alcohol and is stable in bright sunlight. The presence of a little free dehydroundecenoic acid in the ester results in the formation of a grey silver derivative which rapidly darkens in daylight.

Sodium derivatives of acetylenic compounds are not so readily prepared as the silver derivatives, but by the action of finely powdered sodamide upon ethyl dehydroundecenoate in toluene we obtained the sodium derivative of dehydroundecenoamide. The action of this compound upon alkyl halides was similar to that of the silver derivative.

EXPERIMENTAL.

Bromination of Undecenoic Acid.—Light petroleum (b. p. 60—80°) was treated with a slight excess of bromine, washed after some time with sodium bisulphite solution and with water, dried, and distilled. To a solution of 170 g. of undecenoic acid (m. p.

24·5°; b. p. 168·3°/15 mm.) in 500 c.c. of the solvent, cooled in a freezing mixture, 150 g. of bromine were added during 1½ hours with efficient stirring. After 1 hour the precipitate was filtered off, washed with 100 c.c. of cold solvent, and dried (250 g.; m. p. 38·5°). The remainder of the dibromo-acid was obtained as an oil after washing the filtrate with a solution of sodium bisulphite and then with water and drying and evaporating the solvent. The yield of oil was practically the same in a number of brominations (Found: Br, 46·2; equiv., by titration with alkali, 345·1. Calc. for $C_{11}H_{20}O_2Br_2$: Br, 46·5%; equiv., 344·0).

Preparation of Ethyl Dehydroundecenoate and its Silver Derivative.—Dehydroundecenoic acid was prepared from the dibromo-acid by Krafft's method (*loc. cit.*) and esterified with lime-dried alcohol and concentrated sulphuric acid. The ester had b. p. 145°/15 mm.

(*a*) A solution of 2 g. of the ethyl ester in 5 c.c. of absolute alcohol was added to 3·24 g. of silver nitrate in 105 c.c. of alcohol; 4·7 g. of the silver derivative were obtained. The filtrate and washings (10 c.c.) were shaken with solid potassium chloride and filtered. The filtrate required for neutralisation 9·0 c.c. of *N*-sodium hydroxide.

(*b*) 17·5 G. of the ester, 28·4 g. of silver nitrate, and 1 l. of alcohol gave 38·5 g. of the silver derivative, and the filtrate required 82·1 c.c. of *N*-alkali (Found: Ag, 44·5. Calc. for $C_{13}H_{21}O_2Ag,AgNO_3$: Ag, 44·3%).

Action of the Silver Derivative upon Heptyl Bromide in Alcohol.—The silver derivative precipitated from 17·5 g. of the ester was washed and dissolved in 300 c.c. of warm alcohol, 30 g. of heptyl bromide were added, and the solution was warmed under reflux on the water-bath; 30 g. of silver bromide separated during 3 hours. Alcohol was distilled from the filtered solution, and the residue fractionated.

Fraction (*a*), boiling below 140°/15 mm., was redistilled and collected up to 168°/760 mm. After it had been warmed with aqueous caustic potash to hydrolyse heptyl bromide and extracted with ether, an oil was obtained. Heptyl alcohol was removed from this by treatment with successive quantities of sodium. The remaining liquid was distilled and collected at 165—166°/760 mm. (3·5 g.) (Found: C, 74·65; H, 13·7. Calc. for $C_7H_{15}\cdot O\cdot C_2H_5$: C, 74·9; H, 14·0%).

Fraction (*b*) (16 g.), collected at 145°/15 mm., was ethyl dehydroundecenoate, since it gave after hydrolysis an acid of m. p. 43—44° (Found: C, 72·3; H, 10·2; equiv., by titration, 185·2. Calc. for $C_{11}H_{18}O_2$: C, 72·5; H, 10·0%; equiv., 182·1).

Action of the Silver Derivative upon Heptyl Bromide in Absence of Alcohol.—The silver derivative from 15 g. of the ester was dried in a

vacuum desiccator during 2 days and then warmed with 50 g. of heptyl bromide on the water-bath, the flask being shaded. The cooled solution was filtered after dilution with ether. The filtrate gave a fraction, b. p. 95—100°/760 mm. On redistilling this, 4·5 g. were collected at 96—98°. Bromine in the cold converted this into an oil, b. p. 105—107°/15 mm. αβ-Dibromoheptane has b. p. 105—107°/15 mm. (Found: Br, 61·5. Calc. for $C_7H_{14}Br_2$: Br, 62·0%).

Formation of the Sodium Derivative.—Ethyl dehydroundecenoate was heated under reflux for about 2 days with toluene in which a 5% excess of finely powdered sodamide was suspended; ammonia was slowly evolved. The flocculent precipitate of the sodium derivative of dehydroundecenoamide was treated with excess of heptyl bromide. Sodium bromide was slowly formed and the filtered solution gave practically the whole of the ethyl dehydroundecenoate.

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CCL.—*Besson's Supposed Phosphorus Suboxide*, P_2O.

By Leslie James Chalk and James Riddick Partington.

Besson describes (*Compt. rend.*, 1897, **124**, 763; 1897, **125**, 1032; 1901, **132**, 1556; compare *Bull. Soc. chim.*, 1900, **23**, 582) the preparation of an oxide, P_2O, (i) by heating phosphoryl chloride with phosphonium bromide, (ii) by the action of a slow stream of air on a solution of phosphorus in carbon tetrachloride, and (iii) by heating a concentrated solution of phosphorous acid with phosphorus trichloride. The identical products are stated to be yellowish-red and stable at 100°, but decomposed in a vacuum at 135° with the evolution of oxygen. Analysis gave about 79% of phosphorus (P_2O requires 79·49%). The substances obtained by Michaelis and Pitsch (*Ber.*, 1899, **32**, 337; *Annalen*, 1900, **310**, 45) by the action of hydrochloric acid on a solution of yellow phosphorus in aqueous-alcoholic potassium hydroxide, and by the action of acetic anhydride on a solution of hypophosphorous acid in glacial acetic acid, were considered by Besson to be largely P_2O contaminated by phosphorus and solid hydrogen phosphide.

Preparation of Besson's Oxide.—10 G. of Kahlbaum's phosphorous

acid were dissolved in 8 g. of water in a flask under a reflux condenser and 50 g. of phosphorus trichloride were added. Hydrogen chloride was steadily evolved and crystals were formed. These consisted of phosphorous acid, and not phosphorus trioxide, as required by the equations given by Besson, *viz.*, $PCl_3 + H_3PO_3 = 3HCl + P_2O_3$, followed by $2P_2O_3 = P_2O + P_2O_5$. On heating for about 15 minutes on a water-bath with shaking, the crystals disappeared and a yellow solid began to separate. On further heating, red particles appeared. A viscous layer settled out which contained most of the deposit, the upper layer being unchanged phosphorus trichloride. Reaction is complete in 6 hours. Besson states that a substance with the appearance of phosphorus pentoxide is formed in the reaction, but this could not be confirmed, neither was a hissing noise observed on adding water to the residue, although heat was evolved by the action of water on unchanged trichloride—if the upper layer is poured off before the addition of water there is practically no evolution of heat.

The product was filtered, washed with cold water according to the directions of Besson, and dried in a vacuum over phosphorus pentoxide for 3 weeks. The filtrate contained phosphorous, phosphoric, and hydrochloric acids, most of the phosphorus being in the form of phosphorous acid. The dry powder was yellowish-red, but contained darker red particles, and was free from chlorine. The yield from 10 g. of phosphorous acid was 0·7 g. In this way, the preparations numbered I, II, III, and VII in the tables were obtained.

Action of Phosphorus Trichloride on Crystalline Phosphorous Acid.—Although the preceding experiment was performed exactly as specified by Besson, it was clear that it would be better to use crystalline phosphorous acid instead of the solution. 50 G. of phosphorus trichloride and 10 g. of solid phosphorous acid did not react until the mixture was warmed; the acid then dissolved completely and a yellow solid soon appeared. This turned redder on further heating for 5 or 6 hours, and the product was then isolated and dried as before. It was exactly similar in appearance to the previous product. The liquid poured off from the solid was mainly unchanged trichloride (43 g.). The yield of "oxide" was about the same as in the first method. The preparations numbered IV, V, VI, and VIII were obtained by this method. Preparation V, containing 86·7% of phosphorus, was not further examined.

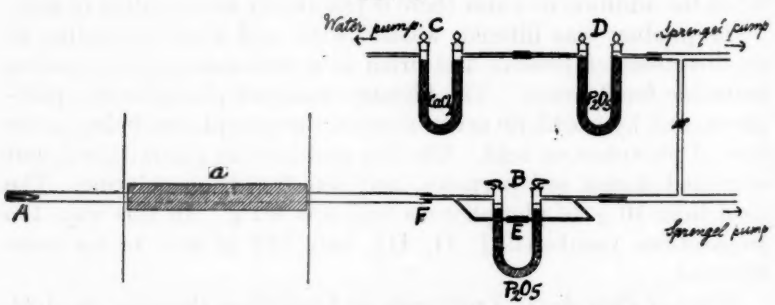
The Action of Phosphorus Trichloride on Phosphorous Acid below 70°.—50 G. of phosphorus trichloride and 10 g. of phosphorous acid were heated so that the temperature never rose beyond 70°. The action was slow, but no further yield appeared after 20 hours. Only 0·15 g. of product resulted, which was pure yellow without any tinge

of orange, and appeared homogeneous under the microscope. The washings contained phosphorous acid and a small amount of phosphoric acid, but no hypophosphorous acid. The upper layer yielded 33·5 g. of unchanged trichloride. The dry powder, specimen IX, had a stronger odour of phosphine than that prepared at 100°.

Analysis of the Products.—The preparations were analysed by the method described by Chapman and Lidbury (J., 1899, **75**, 973), except that phosphoric acid was estimated by the method described by Treadwell (" Quantitative Analysis," p. 437).

The water and hydrogen contents of the preparations were determined by a modification of the apparatus described by Burgess and Chapman (J., 1901, **79**, 1235), which is shown in Fig. 1. The aluminium foil used by these experimenters was omitted. The substance was weighed into a small tube, A, which was introduced

FIG. 1.



into the Bohemian-glass tube, F, 9 mm. in diameter and 120 cm. long. The part inside the resistance furnace, *a*, contained a roll of bright copper gauze. The whole apparatus was first thoroughly cleaned and dried by prolonged heating in a vacuum. The junction with the phosphorus pentoxide absorption tube, B, was made with sealing wax, since this part remained quite cool, so that the tube B could be removed easily for weighing. A screw-clip on the pressure tubing, E, enabled the tube B to be evacuated independently of the tube AF. The substance in A darkened on heating and evolved gas, which was collected in the receiver of the Sprengel pump exhausting the apparatus. When no further gas collected and a vacuum was re-established, the apparatus was allowed to cool and disconnected, and the tubes A and B were weighed. The tube A contained a dark grey residue, sometimes containing white, opaque specks, which were not glassy. Practically the whole of the phosphorus content of this residue could be extracted by boiling water, but the undissolved residue was in every case analysed for phosphorus.

When the preparations were heated with water in a sealed tube for 8 hours at 100°, and the tube was opened under mercury, only a very small diminution in volume was noticed, and the solution was found to contain phosphorous, but not hypophosphorous, acid. Besson attributed the production of phosphorous acid in this experiment to oxidation of P_2O : $P_2O + O_2 + 3H_2O = 2H_3PO_3$, the absorption of oxygen being inferred from a diminution of pressure; he also noticed a smell of phosphine. We find no such diminution of pressure, and there can be no doubt from this and from the quantitative experiments described below that the phosphorous acid is present as such in the original preparations. On further heating the residue from this experiment with water, more phosphorous acid was obtained, but in diminished amount, and an adsorption phenomenon is indicated. The presence of uncombined water in the preparations is considered improbable, since a portion of preparation III, on being kept in a vacuum over phosphorus pentoxide for 2 months, gave practically the same results for water and hydrogen on distillation (0·1 g. gave 0·0142 g. of residue with 43% P, 2·2 c.c. of hydrogen and 0·0056 g. of H_2O) as the freshly dried preparation. The probable constituents of the preparations are therefore: free phosphorus, phosphorous acid, and solid hydrogen phosphides. The preparation made below 70° may be expected to contain more solid phosphides, since a slow reaction between phosphorus trichloride and phosphorous acid in the cold is said to give these substances, whilst at higher temperatures (170°) red phosphorus is said to be the only product.

We assume that the only primary constituents of the preparations are phosphorous acid and phosphorus, the amount of the former being directly estimated from the phosphoric acid in the residue left after distillation in a vacuum. The weight of water and the volume of hydrogen obtained on distillation in vacuum can then be compared with those calculated from the equation: $8H_3PO_3 = 3P_2O_5 + 9H_2O + 2P + 3H_2$. The phosphorus content of the residue was generally above 40%, whereas that of metaphosphoric acid is 38·8% and that of phosphorus pentoxide 43·7%. That the residue should consist mainly of phosphorus pentoxide rather than metaphosphoric acid might appear improbable, but the pentoxide may be produced by the prolonged heating in vacuum of free phosphorus and metaphosphoric acid: $10HPO_3 + 2P = 6P_2O_5 + 5H_2$. The results of the distillation experiments, as is seen from Table I, are in agreement with this hypothesis, except that the hydrogen obtained from the oxide prepared below 70° was greater than the calculated amount, a result which would be expected if solid hydrogen phosphides are present. In other cases, the hydrogen calculated is only slightly

lower than the experimental value, which may indicate the presence of a little solid hydrogen phosphide (compare Burgess and Chapman, *loc. cit.*). The dark colour of the residue obtained on heating in a vacuum is probably due to a trace of free carbon derived from organic matter introduced from the cork of the flask in the preparation of the "oxide." This was estimated by difference on the assumption that the remainder of the residue was phosphorus pentoxide, and it was always very small.

In all cases the gas collected from 0·1 g. of preparation was 2—4 c.c. It was shown to be hydrogen by explosion with oxygen. No contraction was observed with the gas, before or after explosion, in contact with dilute acid or alkali. The contraction on explosion was slightly less than the calculated, although no gas except hydrogen could be detected by qualitative tests. The alleged evolution of oxygen on heating the substance was negatived by experiments in which the copper gauze was omitted. The gas collected in this case was phosphine; it suffered no contraction in contact with alkaline pyrogallol, and on explosion with oxygen gave white fumes of phosphoric acid. The phosphorus contents of the various preparations were as follows :

Preparation.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
% P.	85·1	86·0	86·8	81·1	86·7	86·2	88·8	88·2	87·6

These results definitely exclude the composition P_2O.

In Table I, column 2 gives the actual amount of oxide used in the analysis. The figures in the remaining columns, however, have been calculated to 0·1 g. of oxide for the purpose of comparison. This applies also to all the figures in Tables II and III.

TABLE I.

Effect of distillation of the preparations.

Prep. No.	Weight (g.).	Residue (g.).	H_2O (g.).	Gas (c.c.).	H_2 (c.c.).	H_2O (calc.) (g.).	H_2 (calc.) (c.c.).
I	0·0950	0·0160	0·0059	2·8	2·6	0·0054	2·2
II	0·1081	0·0155	0·0065	3·0	2·9	0·0057	2·4
III	0·1060	0·0135	0·0051	2·2	2·0	0·0050	2·1
IV	0·0987	0·0176	0·0074	3·5	3·2	0·0064	2·7
VI	0·0945	0·0149	0·0063	2·5	2·5	0·0054	2·3
VII	0·0993	0·0121	0·0050	1·7	1·5	0·0044	1·8
VIII	0·1058	0·0128	0·0055	2·1	1·9	0·0047	2·0
IX	0·0595	0·0116	0·0044	4·6	4·4	0·0034	1·4

Specimen IV still contained phosphorous acid which could be extracted by washing. Specimens VII and VIII were washed for a longer time than the others and the phosphorus content is higher, indicating a more complete removal of phosphorous acid. Only 0·0595 g. of Specimen IX was available for distillation.

Table II contains the analyses of the residues left after distillation. Except in the cases of Preparations I and IX, all the phosphorus (as phosphoric acid) was extracted by boiling water. In these two cases, the residues after extraction contained 0·0010 g. and 0·0008 g. of free phosphorus, respectively (compare Burgess and Chapman, *loc. cit.*). The fifth column gives the amount of phosphorous acid equivalent to the phosphorus contained in the residue as P_2O_5, the sixth the amounts of hydrogen and oxygen equivalent to this, *viz.*, $(H_3PO_3)\times(51/82)$. The last column contains the sum of the weights of phosphorus, hydrogen, carbon, and oxygen in 0·1 g. of preparation, *i.e.*, the sum of the figures in columns 4, 6, and 7, and is equal to 0·1 to within 2%. This supports the hypothesis that the supposed oxide P_2O contains free phosphorus and phosphorous acid only.

TABLE II.

Composition of residue after distillation.

Prep. No.	Weight g.	% P in residue.	C. (calc.).	H_3PO_3 equiv. to P extracted.	H and O as H_3PO_3.	P in 0·1 g. "oxide."	Total.
I	0·0160	38·4	0·0009	0·0217	0·0135	0·0851	0·0995
II	0·0155	42·0	0·0005	0·0230	0·0143	0·0860	0·1008
III	0·0135	42·2	0·0006	0·0201	0·0125	0·0868	0·0999
IV	0·0176	42·0	0·0007	0·0261	0·0162	0·0811	0·0980
VI	0·0149	42·2	0·0005	0·0222	0·0138	0·0862	0·1005
VII	0·0121	41·5	0·0006	0·0177	0·0110	0·0888	0·1004
VIII	0·0128	42·5	0·0004	0·0192	0·0119	0·0882	0·1005
IX	0·0116	37·2	0·0009	0·0139	0·0086	0·0876	0·0971

The percentage of phosphorus in Preparations VII and VIII corresponds very nearly with that in the supposed suboxide P_4O, but the behaviour on distillation in a vacuum is different. Burgess and Chapman (*loc. cit.*) found that 0·1 g. of the supposed P_4O gave on distillation about 10 c.c. of hydrogen and left practically no residue, whereas these preparations give only 1—3 c.c. of hydrogen and leave 12% of residue. Burgess and Chapman, however, decomposed the water vapour by heated aluminium.

From the experimentally determined values of phosphorus, oxygen, and hydrogen in the supposed oxide, a formula for the latter may be calculated. This is done in Table III, in which the total should be 0·1 g. This is seen to be the case within 2%. The oxygen is calculated on the assumption that the phosphorus extracted by hot water from the residue after distillation existed as pentoxide.

The properties of the supposed oxide are similar to those of scarlet amorphous phosphorus and of the supposed solid hydrogen phosphides. It is insoluble in water, alcohol, benzene, chloroform, or ether. Dilute nitric acid dissolves it at 40°, whilst concentrated nitric acid causes inflammation. Hydrogen peroxide and sodium

TABLE III.

Prep. No.	P (obs.).	H_2O (obs.).	O (calc.).	H (obs.).	C (obs.).	Total.	Formula.
I	0·0851	0·0059	0·0079	0·0002	0·0009	0·1000	$P_2O_{0\cdot58}H_{0\cdot65}$
II	0·0860	0·0065	0·0084	0·0003	0·0005	0·1017	$P_2O_{0\cdot64}H_{0\cdot70}$
III	0·0868	0·0051	0·0073	0·0002	0·0006	0·1000	$P_2O_{0\cdot55}H_{0\cdot53}$
IV	0·0811	0·0074	0·0095	0·0003	0·0007	0·0990	$P_2O_{0\cdot77}H_{0\cdot68}$
VI	0·0862	0·0063	0·0081	0·0002	0·0005	0·1013	$P_2O_{0\cdot62}H_{0\cdot67}$
VII	0·0888	0·0050	0·0065	0·0001	0·0006	0·1010	$P_2O_{0\cdot46}H_{0\cdot46}$
VIII	0·0882	0·0055	0·0070	0·0002	0·0004	0·1013	$P_2O_{0\cdot52}H_{0\cdot55}$
IX	0·0876	0·0044	0·0056	0·0004	0·0009	0·0989	$P_2O_{0\cdot42}H_{0\cdot63}$

hypochlorite solution oxidise it to colourless solutions containing phosphoric acid. Concentrated ammonia turns it slightly darker in colour, the original colour being restored by exposure to air or by the action of acids. Alcoholic potassium hydroxide forms a dark red solution with evolution of phosphine, the solution being similar to that formed by the supposed suboxide P_4O (as was found by trial).

The mechanism of the formation of Besson's substance (which is really of variable composition) is probably as follows. The phosphorous acid may be decomposed with evolution of phosphine. The latter is known to react with phosphorus trichloride giving, according to the conditions, solid hydrogen phosphide or phosphorus. When prepared at lower temperatures, the product may contain appreciable amounts of solid hydrogen phosphide. It is also possible that phosphorus trioxide may be formed by the action of the trichloride on phosphorous acid (Abegg, "Handbuch," III, iii, 420; the reference to Krafft and Neumann, *Ber.*, 1901, **34**, 566, there given does not appear to be relevant). The trioxide might then decompose, either alone or by interaction with phosphorus trichloride, to form phosphorus or solid hydrogen phosphides.

Summary.

The supposed oxide of phosphorus, P_2O, formed by the action of phosphorus trichloride on phosphorous acid under the conditions described by Besson has neither the composition nor properties attributed to it by that investigator. It is somewhat variable in composition and appears to be a mixture of finely divided amorphous phosphorus with strongly adsorbed phosphorous acid, although, especially when prepared at lower temperatures, solid hydrogen phosphides may be present. The amount of oxygen present is always much less than is required by the formula P_2O, and hydrogen also is always present, even after prolonged drying over phosphorus pentoxide.

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CCLI.—*Syntheses of Glucosides. Part I. The Synthesis of Indican.*

By ALEXANDER ROBERTSON.

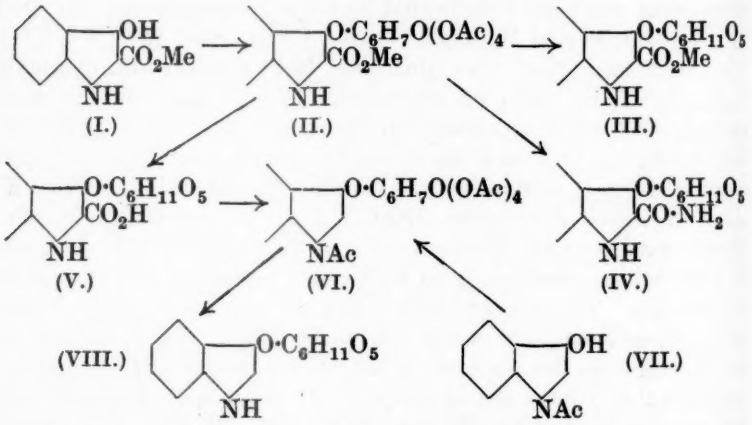
THE glucoside indican, 3-β-glucosidoxyindole, was first isolated by Schunk (*Phil. Mag.*, 1855, **10**, 74; 1858, **15**, 127) from *Polygonum tinctorium*, who stated that the indigotin-yielding substance in *Isatis tinctoria*, "woad," was the same. It was, however, not until many years afterwards that its correct formula was indicated by Marchlewski and Radcliffe (*J. Soc. Chem. Ind.*, 1898, **17**, 434), who suggested that the glucoside had possibly the formula $C_{14}H_{17}O_6N$, and that, on hydrolysis, glucose and indoxyl were formed, the latter on oxidation being converted into indigotin. The proof that indican is an indoxyl glucoside, and that the sugar obtained from it is glucose, was supplied by Hazewinkel (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, **2**, 512). About the same time, Hoogenwerff and ter Meulen (*ibid.*, p. 520) isolated the glucoside in a crystalline condition from *Polygonum tinctorium* and *Indigofera leptostachya*. They showed that it had the formula $C_{14}H_{17}O_6N$ and when crystallised from water contained $3H_2O$. By hydrolysis of the glucoside in the presence of air, they obtained slightly impure indigotin; and later the identity of the sugar with *d*-glucose was indicated by ter Meulen (*Rec. trav. chim.*, 1905, **24**, 444). Beyerinck (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, **3**, 101) showed that the glucoside in *Polygonum tinctorium* is not the same as the indigo-yielding substance in *Isatis tinctoria* as claimed by Schunk, and also that indican was slowly hydrolysed by emulsin, as well as by its specific enzyme, indemulsin.

Perkin and Bloxam (J., 1907, **91**, 1715), Perkin and Thomas (J., 1909, **95**, 793), and Thomas, Bloxam, and Perkin (J., 1909, **95**, 824), working with improved methods, isolated the crystalline glucoside from *Indigofera leptostachya*, *I. sumatrana*, *I. arrecta*, and *Polygonum tinctorium*, and confirmed in detail the work of Hoogenwerff and ter Meulen, Hazewinkel, and Beyerinck. In addition, these workers obtained the glucoside in the anhydrous state. From a study of the hydrolysis of methylated indican, Macbeth and Pryde (J., 1922, **121**, 1660) showed that the glucoside is in all probability a normal β-derivative. This is in agreement with the conclusions arrived at by ter Meulen (*loc. cit.*) as a result of a study of the hydrolysis of the glucoside by enzymes.

In attempting the synthesis of indican, the most obvious method was to obtain the penta-acetyl derivative by the interaction of 1-acetyl-3-hydroxyindole and tetra-acetyl-α-glucosidyl bromide in

acetone solution in the presence of aqueous alkali. Reference to the literature indicated the difficulty of preparing a sufficient quantity of the acetylhydroxyindole, and the instability of the latter in the presence of alkali. Accordingly, another method for the synthesis of the glucoside was devised.

Methyl 3-O-*tetra-acetyl*-β-*glucosidoxyindole*-2-*carboxylate* (II) was obtained in good yield by the interaction of methyl 3-hydroxyindole-2-carboxylate (I) and tetra-acetyl-α-glucosidyl bromide in acetone solution in the presence of potassium hydroxide.



This penta-acetyl glucoside on hydrolysis with methyl-alcoholic potash yielded 3-β-*glucosidoxyindole*-2-*carboxylic acid* (V), which was conveniently isolated from the reaction mixture as the potassium salt. The latter, when treated with fused sodium acetate and acetic anhydride, first on the water-bath and then at 160°, was acetylated and the carboxyl group simultaneously eliminated with the formation of 1-*acetyl*-3-O-*tetra-acetyl*-β-*glucosidoxyindole* (VI). In order to verify the constitution of this substance, a small quantity of it was prepared directly by the interaction of 1-acetyl-3-hydroxyindole (VII) (D.R.-P. 108761) and tetra-acetyl-α-glucosidyl bromide in a cooled acetone solution in the presence of potassium hydroxide. The specimens of *penta-acetylindican* thus obtained were identical. The penta-acetyl glucoside was deacetylated with methyl-alcoholic ammonia, and 3-β-*glucosidoxyindole*, indican (VIII), obtained in good yield. The properties of the synthetic glucoside were identical with those of the natural product described in detail by Perkin and his collaborators (*loc. cit.*).

Hydrolysis of the synthetic indican under various conditions gave the same products as those obtained by these authors, by Hazewinkel (*loc. cit.*) and by Beyerinck (*loc. cit.*).

On deacetylation of the glucoside (II), a mixture of *methyl* 3-β-*glucosidoxyindole*-2-*carboxylate* (III) and 3-β-*glucosidoxyindole*-2-*carboxylamide* (IV) was obtained, but the latter could not be isolated in a crystalline condition. Hydrolysis and acetylation, however, established the nature of the uncrystallised syrup.

The preparation of methyl 3-hydroxyindole-2-carboxylate (Vorländer, *Annalen*, 1898, **301**, 349) was carried out by the method described for the preparation of the corresponding ethyl ester (D.R.-P. 105495). This methyl ester on acetylation yielded an O-*acetyl* derivative.

Experimental.

Methyl 3-*Hydroxyindole*-2-*carboxylate* (I). — To pulverised sodium (2·7 g.) and methyl phenylglycine-*o*-carboxylate (25 g.) in benzene (100 c.c.), one drop of anhydrous methyl alcohol was added and the mixture was gently warmed on the steam-bath until a vigorous reaction set in; the sodium derivative of methyl 3-hydroxyindole-2-carboxylate was then deposited as a solid. When this reaction had almost ceased, the mixture was heated under reflux for 30 minutes and then cooled. The sodium derivative was collected, washed with benzene, dried, and dissolved in ice-water (250 c.c.), and the solution was filtered after treatment with charcoal and acidified with acetic acid (50%). The indoxylic ester thus precipitated crystallised from methyl alcohol (70%) (charcoal) in elongated, glistening needles, m. p. 157—158°. Yield, 15 g.

Methyl 3-*acetoxyindole*-2-*carboxylate* was obtained in almost theoretical yield when methyl 3-hydroxyindole-2-carboxylate (2 g.), fused sodium acetate (2 g.), and acetic anhydride (10 c.c.) were heated under reflux for 1 hour. Water was added to the cooled mixture, and the *acetyl* derivative gradually crystallised. After recrystallisation from methyl alcohol (50%) and then from benzene–ligroin (1 : 9), it was obtained in glistening, elongated prisms, m. p. 145° (Found: C, 62·1; H, 4·7. $C_{12}H_{11}O_4N$ requires C, 61·8; H, 4·7%). It is insoluble in dilute alkali solution. Attempts to obtain a diacetyl derivative were unsuccessful.

Methyl 3-*Tetra-acetyl*-β-*glucosidoxyindole*-2-*carboxylate* (II).—A cooled solution of potassium hydroxide (2·8 g.) in water (20 c.c.) was gradually added to one of methyl 3-hydroxyindole-2-carboxylate (9·3 g.) and tetra-acetyl-α-glucosidyl bromide (20·5 g.) in pure acetone (90 c.c.) cooled to 10°; the acetyl glucoside soon began to crystallise. After remaining at room temperature for 4 hours, the mixture was diluted with water (50 c.c.) and cooled in ice, and the solid was collected and recrystallised from hot methyl alcohol (charcoal). The *acetyl glucoside* was thus obtained in colourless

prisms with blunt ends, m. p. 229—230° (Found: C, 55·5; H, 5·2. $C_{24}H_{27}O_{12}N$ requires C, 55·5; H, 5·2%). Yield, 16·5 g.

This glucoside is sparingly soluble in ether and in cold alcohol, and moderately easily soluble in hot alcohol. A penta-acetyl derivative could not be obtained.

3-β-*Glucosidoxyindole-2-carboxylamide* (IV).—Dry methyl alcohol (200 c.c.) containing finely powdered methyl 3-tetra-acetyl-β-glucosidoxyindole-2-carboxylate (3 g.) in suspension was saturated at 0° with dry ammonia gas. The glucoside gradually dissolved and the solution was allowed to remain at 0° for 14 hours. After removal of the ammonia and methyl alcohol in a vacuum at 18°, the residual oil was freed from acetamide by distillation of the latter at 100°/1—2 mm. The straw-coloured syrup which remained was dissolved in water, and the solution on evaporation in a vacuum desiccator deposited the *amide* as a white solid. This crystallised from water in colourless, rectangular plates, which decomposed at 254—256° to a black mass after darkening at 245° (Found: C, 50·7; H, 5·6; N, 7·5. $C_{15}H_{18}O_7N_2$ requires C, 50·8; H, 5·6; N, 7·8%). Yield, 0·3 g. The amide is fairly soluble in alcohol and in hot water.

The filtrate after the separation of the amide was evaporated to small bulk, and a straw-coloured syrup obtained which could not be induced to crystallise. This undoubtedly consisted of impure *methyl* 3-β-*glucosidoxyindole-2-carboxylate* (III). When this syrup was heated to boiling with 6% hydrochloric acid for 1 minute, methyl 3-hydroxyindole-2-carboxylate (I) crystallised, m. p. 157—158° after recrystallisation from 70% methyl alcohol. The acetyl derivative, m. p. 145°, was identical with that described above. The syrup (1 part) was acetylated by heating it under reflux for 1 hour with fused sodium acetate (1 part) and acetic anhydride (10 parts). Water was added to the cooled mixture to decompose the excess of acetic anhydride, and methyl 3-tetra-acetyl-β-glucosidoxyindole-2-carboxylate separated, m. p. 229—230° after recrystallisation from methyl alcohol. A mixture of the latter with an authentic specimen of the acetylated glucoside showed no depression of the melting point.

3-β-*Glucosidoxyindole-2-carboxylic Acid* (V).—A solution of potassium hydroxide (4 g.) in 80% methyl alcohol (25 c.c.) was gradually added to a suspension of methyl 3-tetra-acetyl-β-glucosidoxyindole-2-carboxylate in methyl alcohol (50 c.c.). After the solid had dissolved, the solution was kept at room temperature for 12 hours, methyl alcohol (20 c.c.) was then added, and the mixture heated under reflux on the water-bath for 2 hours, during which time the potassium salt of 3-β-glucosidoxyindole-2-carboxylic acid crystallised

out. When cold, the colourless potassium salt was collected, washed with dry methyl alcohol, and dried. The salt (yield, 3·5 g.) was sufficiently pure for use in the next stage of the synthesis.

A solution of the potassium salt (1 g.) in water (4 c.c.) was acidified with a slight excess of 2% hydrochloric acid. The pale blue, crystalline precipitate of the *glucoside* which separated was collected and recrystallised from warm water (charcoal), from which it separated in almost colourless, rod-like prisms, which turned brown at 215—220° and decomposed to a dark liquid at 230—231° (Found: C, 53·1; H, 5·1; N, 4·0. $C_{15}H_{17}O_8N$ requires C, 53·1; H, 5·0; N, 4·1%).

A solution of this glucoside in dilute hydrochloric acid, containing ferric chloride, on boiling is quickly decomposed with the formation of indigotin. An aqueous solution when heated to boiling quickly assumes a blue colour, due to slight hydrolysis and the formation of a trace of indigotin.

1-*Acetyl*-3-*tetra-acetyl*-β-*glucosidoxyindole* (*Penta-acetylindican*) (VI).—(*A.*) Potassium 3-β-glucosidoxyindole-2-carboxylate (3·5 g.), fused sodium acetate (3·5 g.), and acetic anhydride (45 c.c.) were heated on the steam-bath for 2 hours, and then at 160—162° for 1 hour. Water (200 c.c.) was added to the cooled mixture; the penta-acetylindican then separated as an oil which gradually solidified. The solid was repeatedly crystallised from methyl alcohol (charcoal) to free it from coloured impurities, and finally from ethyl alcohol, from which it separated in glistening, colourless, elongated, rectangular prisms, m. p. 148° (yield, 4·0 g.) (Found: C, 57·2; H, 5·4. $C_{24}H_{27}O_{11}N$ requires C, 57·0; H, 5·3%). Penta-acetylindican is slightly soluble in cold and easily soluble in hot alcohol, and readily soluble in cold chloroform.

(*B.*) A suspension of methyl 3-tetra-acetyl-β-glucosidoxyindole-2-carboxylate (6 g.) in 5% baryta water (200 c.c.), maintained at 40—45°, was vigorously agitated for 24 hours; the solid gradually dissolved. The excess of barium hydroxide was precipitated by carbon dioxide, the barium carbonate removed, and the filtrate evaporated to dryness. The residue was acetylated and *penta-acetylindican* isolated, m. p. 148°, as described above. Yield, 0·8 g.

(*C.*) A solution of potassium hydroxide (0·84 g.) in water (10 c.c.) was gradually added to one of 1-acetyl-3-hydroxyindole (VI) (*loc. cit.*) (2·1 g.) and tetra-acetyl-α-glucosidyl bromide (6·2 g.) in 100 c.c. of acetone maintained below 5° in an atmosphere of nitrogen. The mixture was kept in the ice-chest for 5 hours and then acidified with dilute acetic acid, and the acetone was removed in a vacuum at room temperature. The dark brown residual oil was dissolved in warm methyl alcohol (20 c.c.), and the solution

poured into cold water (300 c.c.); impure penta-acetylindican was then precipitated in a semi-solid condition. The glucoside crystallised from ethyl alcohol (charcoal) in glistening, colourless, elongated, rectangular prisms, m. p. 148° (yield, 0·7 g.) (Found: C, 56·8; H, 5·3; N, 2·8. $C_{24}H_{27}O_{11}N$ requires C, 57·0; H, 5·3; N, 2·6%). A mixture of the penta-acetylindican prepared in this way with that described above showed no depression of the melting point.

3-β-*Glucosidoxyindole* (*Indican*) (VIII).—1-Acetyl-3-tetra-acetyl-β-glucosidoxyindole (8 g.) quickly dissolved in absolute methyl alcohol (300 c.c.) saturated at room temperature with dry ammonia. After 24 hours, the solution was cooled to 0°, saturated with ammonia, and kept for 12 hours. The ammonia and methyl alcohol were then removed under diminished pressure at 20—25°, and the residual syrup was freed from acetamide by exposure to a high vacuum (1—2 mm.) for 1 hour at 100°. A solution of the green residue in warm water (30 c.c.) was filtered after treatment with charcoal, and exposed to a vacuum over soda–lime and calcium chloride. An almost colourless mass of crystalline indican gradually filled the liquid. Yield, 4·2 g.

The glucoside, after being twice recrystallised from water, was obtained as a mass of colourless, silky needles, m. p. 57—58°. When dried in a vacuum over sulphuric acid for 48 hours, indican lost part of its water of crystallisation; it then melted at 100—101°, became crystalline at 160°, and finally melted at 176—178°. It was obtained anhydrous, m. p. 176—178°, by heating it in the steam-oven for 3 hours, at 110° for 1 hour, and finally at 160° for 5 minutes (Found in a specimen crystallised from water and air-dried: C, 48·2; H, 6·5; N, 4·4; H_2O, 15·8. Calc. for $C_{14}H_{17}O_6N,3H_2O$: C, 48·1; H, 6·6; N, 4·0; H_2O, 15·5%. Found in an anhydrous specimen: C, 56·6; H, 6·0; N, 5·0. Calc. for $C_{14}H_{17}O_6N$: C, 56·9; H, 5·8; N, 4·8%). Anhydrous indican was also obtained from the hydrated variety in colourless prisms, m. p. 176—178°, by crystallisation from warm absolute ethyl alcohol–benzene as described by Perkin and Bloxam (*loc. cit.*).

Synthetic indican is rapidly hydrolysed in warm 3% hydrochloric acid with the liberation of glucose and indoxyl, which in the presence of acid forms "indoxyl brown." If, however, a little ferric chloride is added as an oxygen carrier and air is bubbled through the solution, the liberated indoxyl is instantaneously oxidised to almost pure indigotin. When a drop of concentrated hydrochloric acid is added to a solution of the glucoside in warm glacial acetic acid containing a little *p*-nitrosodimethylaniline as an oxidising agent, glistening leaflets of indigotin, which have a bronze reflex, quickly separate. Hydrolysis of the glucoside in warm 3%

hydrochloric acid in the presence of isatin gives a quantitative yield of indirubin, which separates in microscopic red prisms, whilst, with *p*-nitrobenzaldehyde, the liberated indoxyl forms *p*-nitrobenzaldehydeindogenide, which crystallises from acetone in red, prismatic needles, m. p. 273—274°.

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CCLII.—*Reactions of Displacement in the Tropic Acid Group. Part II.*

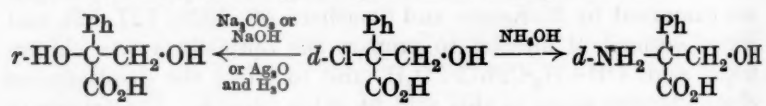
BY CARL ALOYSIUS KERR.

IN Part I, the action of sodium carbonate and of concentrated aqueous ammonia on *l*-β-chlorohydratropic acid, $CH_2Cl{\cdot}CHPh{\cdot}CO_2H$, was examined by McKenzie and Strathern (J., 1925, **127**, 82), and it now seemed of interest to prepare the optically active chlorotropic acid, $OH{\cdot}CH_2{\cdot}CPhCl{\cdot}CO_2H$, and to effect the displacement of the chlorine atom in this acid by other groups. The actions of alkali, moist silver oxide, ammonia, and reducing agents on both the active and the inactive acid were marked out for study. Moreover, the displacement of chlorine by hydrogen obviously called for inquiry, since such a change has been investigated only rarely in connexion with the Walden inversion, for example, in the reduction of *l*-chloromalic acid to *d*-malic acid (Kuhn and Zell, *Ber.*, 1926, **59**, 2514).

The preparation of *r*-chlorotropic acid is described by Ladenburg and Rügheimer (*Ber.*, 1880, **13**, 373), who acted on atropic acid with a dilute solution of hypochlorous acid, prepared by passing chlorine into a suspension in water of freshly precipitated, yellow mercuric oxide. The author has found that this acid can be more conveniently prepared by the action of monochlorourea on atropic acid, according to the equation $CH_2{:}CPh{\cdot}CO_2H + NH_2{\cdot}CO{\cdot}NHCl + H_2O = OH{\cdot}CH_2{\cdot}CPhCl{\cdot}CO_2H + CO(NH_2)_2$. Monochlorourea has been successfully used by Detœuf (*Bull. Soc. chim.*, 1922, **102**, 176) in the preparation of the chlorohydrins of unsaturated substances, and was found in the present case to give nearly 80% yields of chlorotropic acid. The resolution of chlorotropic acid into its active components can be accomplished by means of morphine, with methyl alcohol as solvent. *d*-Chlorotropic acid has $[\alpha]_D^{18°} = +12{\cdot}6°$ for $c = 3{\cdot}025$ in methyl alcohol, and melts at

123—124°, whereas the *r*-acid has m. p. 129—130°. The rotations of chlorotropic acid in acetone and in water were considerably lower than in methyl alcohol. The first mother-liquor in the resolution contained an excess of the morphine salt of *l*-chlorotropic acid, and by five recrystallisations of this salt from methyl alcohol a morphine salt resulted which gave *l*-chlorotropic acid with $[\alpha]_D^{15°} = -12{\cdot}4°$ in methyl alcohol ($c = 3{\cdot}586$).

The action of sodium carbonate or caustic soda on *r*-chlorotropic acid gave as a main product atroglyceric acid, $OH{\cdot}CH_2{\cdot}CPh(OH){\cdot}CO_2H$, m. p. 144—145°, as well as a small quantity of a neutral oil which corresponded with the formula $C_8H_8O_2$ but could not be identified with the amount in hand. Aqueous ammonia with chlorotropic acid gave, as was expected, a chlorine-free nitrogenous substance, proved to be α-amino-β-hydroxy-α-phenylpropionic acid. *d*-Chlorotropic acid (1 mol.) when treated with moist silver oxide (2 mols.) gave *r*-atroglyceric acid, with only slight formation of the yellow neutral oil noticed in the case of alkali. The following changes can be brought about:



The action of sodium carbonate solution and of moist silver oxide on *d*-chlorotropic acid led to the formation, in both cases, of optically inactive atroglyceric acid. Such complete racemisation was not to be expected, especially in the case of silver oxide, but a similar case of complete racemisation is to be found in the action of water on *l*-α-chloro-α-phenylpropionic acid and of nitrous acid on *l*-α-amino-α-phenylpropionic acid (McKenzie and Clough, J., 1910, **97**, 1016; 1912, **101**, 390), which compounds are closely allied in structure to chlorotropic acid.

The action of concentrated ammonia on *d*-chlorotropic acid gave, on the other hand, a dextrorotatory α-amino-β-hydroxy-α-phenylpropionic acid with $[\alpha]_D^{16°} = +40{\cdot}6°$ ($c = 6{\cdot}208$) in hydrochloric acid solution. The optical purity of the amino-acid was considered to be high, but the complete proof that the optically pure acid was actually isolated was lacking owing to the difficulty of finding a suitable solvent for it. In the displacement of chlorine by the amino-group, no such extensive racemisation took place as in the formation of *r*-atroglyceric acid from *d*-chlorotropic acid. Explanation of the latter racemisation cannot be traced to the rotatory power of atroglyceric acid being low, as this acid is at present being resolved and is known to have a fairly high specific rotation.

The conversion of *r*-chlorotropic acid into tropic acid by means

of reducing agents was not accomplished, and this is in agreement with the work of McKenzie and Wood (J., 1919, **115**, 828), who found that this conversion could not be effected in the manner described by Ladenburg and Rügheimer (*loc. cit*).

Experimental.

Chlorotropic Acid.—Atropic acid, prepared from tropic acid by Raper's method (J., 1923, **123**, 2558), had m. p. 107—108° when recrystallised from methyl alcohol. Monochlorourea was prepared by Detœuf's method (*loc. cit.*) and its strength estimated by titration with potassium iodide and thiosulphate. Atropic acid (27 g.; 1 mol.) was mixed with 135 c.c. of water, containing 2 c.c. of glacial acetic acid, and monochlorourea solution (1½ mols.) was added. With continuous stirring for 24 hours, most of the atropic acid went into solution, the remainder going pasty. The pasty atropic acid was filtered off, washed free from chlorotropic acid with water, and recrystallised from rectified spirit; 8 g. of atropic acid were recovered. The filtrate and washings were acidified with dilute sulphuric acid and sulphurous acid was added until no reaction with starch–iodide paper was shown. The excess of sulphur dioxide was removed by boiling and the solution extracted seven times with ether. Yield, 18 g. of crude chlorotropic acid. In previous work (Ladenburg and Rügheimer, *loc. cit.*; McKenzie and Wood, *loc. cit.*), chlorotropic acid was purified by washing with cold benzene, but it was found better to recrystallise it from chloroform. Yield, 16 g. of chlorotropic acid, m. p. 129—130°.

Attempted Conversion of Chlorotropic Acid into Tropic Acid.—Ladenburg and Rügheimer (*loc. cit.*) record the reduction of chlorotropic acid with zinc and iron filings in concentrated alkali, but McKenzie and Wood (*loc. cit.*) failed to effect the reduction either by this means or by means of sodium amalgam, zinc and hydrochloric acid, or caustic soda and aluminium. 3 G. of chlorotropic acid, made into a paste with 20 g. of moist copper–zinc couple, were treated with concentrated hydrochloric acid and the mixture was heated on a water-bath for 4 hours. The sludge was separated by decanting off the liquid, and then washed with hot water. Four ether extractions of the acid liquor and washings gave a yellow oil which crystallised on standing. After two recrystallisations from hot chloroform, the crystals melted at 117—122°, but a mixture with pure tropic acid (m. p. 117—118°) had a m. p. 90—93°. After heating 3 g. of chlorotropic acid, 10 g. of copper–zinc, and 100 c.c. of hydrochloric acid (4*N*) for 23 hours, and isolating the product as before, 2 g. of white solid, containing chlorine, and of m. p. 114—116°, were isolated from the ethereal extracts. A fractional

crystallisation of this substance from water gave 0·7 g. of chlorotropic acid (m. p. 128—130°). 3 G. of chlorotropic acid, 50 c.c. of water, and an excess of zinc foil were kept in a platinum basin for two months and then treated with an excess of dilute sulphuric acid. The yellow oil obtained by extraction with ether crystallised to give a solid, m. p. 105—117°, which contained chlorine.

Action of Sodium Hydroxide on r-*Chlorotropic Acid.*—3 G. of chlorotropic acid were neutralised with 155 c.c. of caustic soda (*N*/10), and 154 c.c. of caustic soda further added with a drop of phenolphthalein. After 1 hour's heating on the water-bath the colour of the indicator faded. The cooled mixture was made alkaline, and the neutral oil removed by extraction with ether four times. Yield, 0·5 g. The alkaline solution was made acid with dilute sulphuric acid and extracted five times with ether. From the dried ethereal extracts, 1·1 g. of crystalline acid were obtained, which furnished 0·7 g. of an acid, m. p. 141—145°, when recrystallised from hot ethyl acetate. A second recrystallisation from the same solvent gave 0·5 g. of atroglyceric acid, m. p. 145—147°, (Fittig and Kast, *Annalen*, 1881, **206**, 32, give m. p. 146°) (Found: C, 59·3; H, 5·6. Calc., C, 59·3; H, 5·5%).

Action of Sodium Carbonate on r-*Chlorotropic Acid.*—2 G. of chlorotropic acid were neutralised with approximately *N*-sodium carbonate (9 c.c.), a drop of phenolphthalein was added, and a further 8·5 c.c. of sodium carbonate were run in. After 10 minutes on the water-bath, the colour of the indicator was discharged, and boiling was continued for 20 minutes. The cooled mixture, made alkaline, was extracted with ether to remove a small quantity of neutral oil. Five ether extractions of the acidified liquor gave 1 g. of solid, m. p. 130—138°, which, after recrystallisation from water, had m. p. 144—145°. It was chlorine-free and identified as atroglyceric acid.

α-*Amino*-β-*hydroxy*-α-*phenylpropionic Acid.*—A solution of 3 g. of chlorotropic acid in 50 c.c. of concentrated ammonia, saturated at 0°, was kept in a stoppered bottle for 7 days at the ordinary temperature, and then transferred to a crystallising dish. After 16 hours' standing, 2·2 g. of an acid, washed free from ammonium chloride by water, were separated. The acid was chlorine-free, gave no ammonia with caustic alkali, and behaved as an amino-acid, being soluble in acid and in alkali. It was purified by dissolving it in caustic soda and making the solution exactly neutral with hydrochloric acid. A yield of 1·3 g. of pure acid was obtained from 1·4 g. of crude acid. α-*Amino*-β-*hydroxy*-α-*phenylpropionic acid* has m. p. 285—288° (decomp.) and is insoluble in the commoner organic solvents and in water (Found: C, 59·8; H, 6·0. $C_9H_{11}O_3N$

requires C, 59·7; H, 6·1%). Its *hydrochloride* separates in rhombic prisms, m. p. 225° (decomp.).

Preparation of Optically Active Chlorotropic Acid.—A solution of 30 g. of chlorotropic acid in 300 c.c. of hot methyl alcohol was added to a solution of 45 g. of morphine in 3400 c.c. of methyl alcohol, and the mixture heated just to boiling. On cooling, crystallisation began, and after 18 hours the resulting 45 g. of very fine needles were dissolved by heating in 3750 c.c. of methyl alcohol. On concentration to 1850 c.c., the solution, after 48 hours, gave 24 g. of crystals which were dissolved by heating with 2500 c.c. of methyl alcohol. The solution was concentrated to 1250 c.c. and after 24 hours 15 g. of morphine chlorotropate, crystallising in fine needles, were separated. The acid was obtained by acidification with dilute sulphuric acid and extraction with ether. Yield, 5·8 g. with $[\alpha]_D^{18°} = +11{\cdot}2°$ ($c = 3{\cdot}5565$) in methyl alcohol. Three successive crystallisations of this dextro-acid from chloroform gave acids with the following rotations in methyl alcohol: $[\alpha]_D^{17°} = +12{\cdot}0°$ ($c = 3{\cdot}052$), $[\alpha]_D^{18°} = +12{\cdot}5°$ ($c = 3{\cdot}1245$), $[\alpha]_D^{18°} = +12{\cdot}6°$ ($c = 3{\cdot}025$). The pure d-*chlorotropic acid* has therefore $[\alpha]_D^{18°} = +12{\cdot}6°$ ($c = 3{\cdot}025$) in methyl alcohol. It melts at 123—124° (Found: C, 53·8; H, 4·5. $C_9H_9O_3Cl$ requires C, 53·8; H, 4·5%). The first mother-liquor in the resolution was evaporated to small bulk, and 29 g. of morphine salt were separated. This was recrystallised five times from methyl alcohol, and the resulting salt on decomposition gave l-*chlorotropic acid* with $[\alpha]_D^{15°} = -12{\cdot}4°$ ($c = 3{\cdot}586$) in methyl alcohol.

Action of Sodium Carbonate on d-*Chlorotropic Acid.*—1 G. of dextrorotatory chlorotropic acid, with $[\alpha]_D^{16°} = +10{\cdot}3°$ in methyl alcohol, was neutralised with 7·4 c.c. of sodium carbonate (0·5745*N*) and 7·2 c.c. of the alkali were further added, with a drop of phenolphthalein. After heating for 10 minutes on the water-bath, the solution became colourless; it was made alkaline, and the neutral oil removed by extraction with ether. The solution was acidified with dilute sulphuric acid, and the acid extracted with ether. 0·3 G. of chlorine-free solid was obtained. This was atroglyceric acid and it was quite inactive ($c = 2{\cdot}618$) in methyl alcohol.

Action of Silver Oxide on d-*Chlorotropic Acid.*—1 G. (1 mol.) of dextrorotatory chlorotropic acid with $[\alpha]_D^{16°} = +10{\cdot}3$ in methyl alcohol, and the silver oxide obtained from 1·7 g. (2 mols.) of silver nitrate by precipitation with caustic soda, were mixed with 50 c.c. of water and stirred mechanically for 2 hours. After 60 hours at the ordinary temperature, the mixture was heated for ½ hour, and the silver chloride removed by precipitation with hydrochloric acid. By extraction of the filtrate with ether 0·2 g. of solid, m. p. 143—

146°, was obtained. A mixture of this with atroglyceric acid had m. p. 143—145°, and therefore the substance was atroglyceric acid. It was completely inactive ($c = 1{\cdot}764$) in methyl alcohol.

Action of Aqueous Ammonia on d-*Chlorotropic Acid.*—A solution of 1 g. of *d*-chlorotropic acid with $[\alpha]_D^{18^\circ} = +12{\cdot}6^\circ$ in methyl alcohol, in 10 c.c. of concentrated ammonia, saturated at 0°, was kept in a stoppered bottle for 10 days and then transferred to a crystallising dish. After 3 days, all the solvent had evaporated and the remaining solid was washed free from ammonium chloride and dried. Yield, 0·6 g. of α-amino-β-hydroxy-α-phenylpropionic acid. The rotation of the amino-acid was $[\alpha]_D^{16^\circ} = +40{\cdot}6^\circ$ in *N*-hydrochloric acid ($c = 6{\cdot}208$). Failure attended the attempts to raise the rotation of this acid, either by repeated precipitation from its solution in caustic soda by means of hydrochloric acid, or by recrystallisation from concentrated aqueous ammonia. A saturated solution of ammonia in *sec.*-octyl alcohol does not convert chlorotropic acid into the corresponding amino-acid.

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CCLIII.—*Methylmercuric Halides and Hydroxide.*

By LEONARD ERIC HINKEL and THOMAS HUBER ANGEL.

AN attempt to repeat Marvel and Gould's preparation of methylmercuric iodide by the action of magnesium methyl iodide upon an excess of mercuric chloride suspended in ether (*J. Amer. Chem. Soc.*, 1922, **44**, 153) resulted only in the production of the double compound $CH_3{\cdot}HgCl,2CH_3{\cdot}HgI$ and a small quantity of methylmercuric chloride. If the Grignard reagent was added very slowly to the suspension of mercuric chloride, a copious precipitate of mercuric iodide soon formed, which readily dissolved on further addition of the reagent. The formation of mercuric iodide can be explained by assuming that the methylmercuric iodide produced by reaction (1) reacts with the excess of mercuric chloride in accordance with equation (2).

$$CH_3{\cdot}MgI + HgCl_2 = CH_3{\cdot}HgI + MgCl_2 \quad . \quad . \quad . \quad (1)$$

$$2CH_3{\cdot}HgI + HgCl_2 = 2CH_3{\cdot}HgCl + HgI_2 \quad . \quad . \quad . \quad (2)$$

In support of this assumption, it was found that the latter reaction occurs readily in alcoholic or ethereal solution. The subsequent

solution of mercuric iodide on further addition of the Grignard reagent is explained by their interaction as represented by the equation (3).

$$CH_3{\cdot}MgI + HgI_2 = CH_3{\cdot}HgI + MgI_2 \quad . \quad . \quad . \quad (3)$$

This reaction proceeds smoothly and serves as a convenient method for the preparation of methylmercuric iodide in quantity. The fact that the double compound $CH_3{\cdot}HgCl,2CH_3{\cdot}HgI$ was obtained instead of methylmercuric iodide in the repetition of Marvel and Gould's experiment adds further support to the above assumption, since it was observed that from a hot alcoholic solution of methylmercuric chloride and iodide the stable double compound crystallised on cooling. The double compound is converted by mercuric chloride into methylmercuric chloride, and it is probable that the small amount of the latter which was found associated with the double compound in the original reaction product owed its origin to this cause, since the amount formed increased with the excess of mercuric chloride originally employed. From a consideration of these facts, it would appear impossible to obtain methylmercuric iodide under the conditions of Marvel and Gould.

Methylmercuric hydroxide has long been known in solution (Frankland, *Annalen*, 1853, **85**, 368; Dunhaupt, *ibid.*, 1854, **92**, 381; *J. pr. Chem.*, 1854, **61**, 399; Crymble, J., 1914, **105**, 666), but it was first isolated in the solid form by Sneed and Maynard (*J. Amer. Chem. Soc.*, 1922, **44**, 2946) from methylmercuric iodide and moist silver oxide in the presence of a small amount of alcohol.

Sneed and Maynard's method of purification of the base—precipitation from saturated alcoholic solution with a large excess of dry ether—is very wasteful, for large quantities of ether are necessary, the base undergoes much decomposition in its presence, and five repetitions of the process do not effect complete purification (m. p. 104°). A method is now described whereby the purification can be efficiently and rapidly achieved without loss of material. The pure base so obtained differs from that prepared by Sneed and Maynard both in melting point and in solubility.

Experimental.

Action of Magnesium Methyl Iodide on Mercuric Chloride.—The Grignard reagent prepared from 2·4 g. of magnesium was added to 30 g. of finely powdered mercuric chloride suspended in 250 c.c. of dry ether under the conditions described by Marvel and Gould (*loc. cit.*). The crude product was crystallised from hot thiophen-free benzene and then fractionally from methyl alcohol, the less soluble mercuric iodide and methylmercuric chloride being thereby removed; the final product was obtained in small, pearly leaflets, m. p. 129°

(Found: Cl, 4·0; I, 27·1. $C_3H_9ClI_2Hg_3$ requires Cl, 3·8; I, 27·0%). The double compound differs from methylmercuric chloride in having a much more intense and unpleasant odour.

Methylmercuric iodide was prepared under the conditions previously described, mercuric chloride being replaced by the equivalent amount of mercuric iodide. The product crystallised from methyl alcohol in transparent, rectangular plates melting at 145° and not 143° as stated in the literature (Found: I, 36·9. Calc.: I, 37·05%).

Methylmercuric Hydroxide.—Methylmercuric iodide (10 g.) in 50 c.c. of methyl alcohol and 2 c.c. of water was mechanically agitated for 3 hours with 7 g. of moist silver oxide containing 34% of water. The filtered solution was evaporated to dryness in a vacuum at 40°, the white residue warmed to 30° with 20 c.c. of chlorobenzene, in which it was very sparingly soluble, and alcohol added until solution was just effected, the temperature being kept at 30°; the alcohol was then removed in a vacuum over sulphuric acid, and the base, which separated in small crystals, was drained from the chlorobenzene and washed with light petroleum (previously treated with alcoholic potassium hydroxide to remove sulphur compounds, since these react readily with methylmercuric hydroxide). This process of purification was repeated several times; the base then obtained, after drying in a vacuum, melted at 106° (Found, by Rupp and Nöll's method, Meyer's "Lehrbuch der Organisch-Chemischen Methodik," 1922, p. 359: Hg, 86·0. Calc. for CH_4OHg: Hg, 86·2%). The pure base forms white crystals with a pearly lustre having a faint, unpleasant odour. It decomposes slowly on standing, more rapidly in presence of ether. When heated above its melting point, it partly decomposes and then detonates violently. Contrary to the statements of Sneed and Maynard, it is very sparingly soluble in cold benzene, toluene, carbon tetrachloride, and light petroleum.

The authors desire to thank Professor J. E. Coates for his constant help and interest in this investigation.

UNIVERSITY COLLEGE, SWANSEA. [*Received, June 1st*, 1927.]

CCLIV.—*The Alkaloids of* Picralima Klaineana.

By THOMAS ANDERSON HENRY and THOMAS MARVEL SHARP.

IN December, 1923, we received from the Imperial Institute a supply of "Akuamma" seeds which had been forwarded by the Department of Agriculture in the Gold Coast Colony, accompanied by herbarium specimens of the plant, which had been identified

by the Director of the Royal Botanic Gardens, Kew, as those of *Picralima Klaineana*, Pierre. A full account of the botany of the plant and of the use of the seeds as a febrifuge in native medicine has been published by Holmes (*Pharm. J.*, 1915, **41**, 758; 1922, **55**, 478). Last year Frère Just Gillet, Curator of the Botanical Gardens at Kisantu, Belgian Congo, sent us a small supply (300 g.) of seeds which also were identified at Kew as derived from a species of Picralima, probably *P. Klaineana*. In spite of its reputation as the source of a useful drug, at least among African natives, *P. Klaineana* does not seem to be widely distributed and Frère Gillet reports that he had to make a tedious journey of some 30 leagues to collect his small sample. We are therefore the more indebted to the authorities of the Imperial Institute and in particular to the officers of the Department of Agriculture in the Gold Coast Colony, for the supplies of seed we have examined.

Beyond the preliminary work referred to in the articles by Holmes (*loc. cit.*), there appeared, when we began this work, to be no record of the chemical examination of any species of *Picralima*, but two papers have been published recently by Clinquart (*Bull. Acad. Roy. Med. Belge*, 1926, 492; *J. Pharm. Belg.*, 1927, **9**, 187) giving results of a preliminary examination of the seeds, bark and leaves also supplied by Frère Gillet. Clinquart obtained a few centigrams of a crystalline alkaloid, m. p. 242—243°, and a large amount of an amorphous alkaloid. The behaviour of these two alkaloids with the usual precipitants and colour-producing reagents is described, but no attempt is made to characterise either alkaloid or its salts in detail. In view of the publication of these two papers it has been considered desirable to place on record the data now presented. The seeds of *P. Klaineana* contain at least four alkaloids, two of which have been crystallised. Only one of these has so far been obtained in sufficient quantity for characterisation and this, which is no doubt identical with Clinquart's crystalline base, it is proposed to call *akuammine* from "akuamma," one of the native names of *P. Klaineana* in the Gold Coast. Akuammine has the formula $C_{22}H_{28}O_4N_2$, yields a series of well-crystallised salts, gives a number of characteristic colour reactions with aromatic aldehydes in presence of hydrochloric acid, and contains one methoxyl, one hydroxyl, and one methylimino-group. The last probably represents a tertiary nitrogen atom, since akuammine furnishes a well-crystallised *monomethiodide*, which decomposes on heating, evolving a fishy odour, doubtless due to dimethylamine. The alkaloid does not react with semicarbazide or other reagents for carbonyl groups and no evidence of a methylenedioxy-group is afforded with Gaebel's reagent. The state of the remaining nitrogen has not been ascer-

tained; on treatment in hydrochloric acid solution with sodium nitrite, a scarlet hydrochloride is formed, which does not give Liebermann's nitrosoamine reaction and appears to be a nitro-derivative of akuammine. Akuammine is converted by alkalis under certain conditions into a *monohydrate*, which crystallises with some difficulty. The latter is also formed on hydrolysis of acetylakuammine by alkali, and an O-*methyl* derivative of the monohydrate appears to be produced when akuammine is treated with methyl iodide in presence of alkali. One or both of the remaining oxygen atoms are no doubt involved in these changes.

The other three alkaloids, referred to subsequently as A, B, and D, we propose to examine fully as soon as material is available. Names are not suggested for them, as they may prove to be related to akuammine, in which case it may not be necessary to add to the already large trivial nomenclature of alkaloids. Alkaloid D is remarkable in having a specific rotation of $-737°$ in alcohol or chloroform. Neither A nor B has yet been obtained crystalline.

Both the Congo and the Gold Coast seeds yield akuammine and alkaloids A and B, but only one sample of Gold Coast seeds has so far yielded alkaloid D.

EXPERIMENTAL.

The finely ground seeds were extracted in a copper Soxhlet apparatus first with petroleum, b. p. 60—80°, to remove fat and then with 96% alcohol. The alcoholic extract was taken to dryness under reduced pressure, and the residue treated with successive quantities of 2% hydrochloric acid until alkaloid was no longer removed. The mixed acid liquors were shaken out with ether to remove resinous and waxy impurities and then diluted with water until no further precipitation took place. The precipitate at this stage consists of a weakly basic alkaloid or mixture of alkaloids (A), from which no crystalline material has so far been obtained. The filtrate from this was digested with charcoal for 1 hour on a water-bath, filtered, allowed to cool, and then treated with saturated sodium carbonate solution in excess; this precipitated a mixture of alkaloids as a brown powder, which was collected, washed with hot water, and dried in a vacuous desiccator. The dry mixture was then extracted with ether in a Soxhlet apparatus and so separated into a further quantity of material apparently identical with (A), which remained undissolved in the extractor, and a partly crystalline powder, which gradually accumulated in the extraction flask. When the ether ceased to extract alkaloid, the solvent was distilled off and the dry residue macerated with twice its weight of alcohol, which dissolved a second amorphous alkaloid (B), and left a partly

crystalline residue of crude akuammine (alkaloid C). The latter was collected, washed with a little alcohol, allowed to dry in the air, and then treated with a slight excess of *N*-sulphuric acid (2·8 c.c. approx. per gram) and sufficient water to dissolve it on boiling. The hot solution was treated with charcoal and filtered. On cooling, thin, colourless needles (m. p. 214—218°) of crude akuammine sulphate separated. The mother-liquor on concentration in a vacuous desiccator deposited more of the same sulphate, but finally dried up to a brown varnish. From this, by solution in dry alcohol, a further crop of akuammine sulphate can be obtained, but eventually an amorphous residue of the sulphate of alkaloid B is left. If ammonia solution is used in place of sodium carbonate for precipitation, the residue left after the removal of most of the akuammine sulphate sets to a jelly due to the presence of the sulphate of a hydrate of akuammine formed by the action of ammonia on this alkaloid as described later (p. 1958).

The cold alcoholic extract of the ether-soluble portion of the precipitated alkaloids was taken to dryness under reduced pressure, dissolved in sufficient *N*-sulphuric acid to form a faintly acid solution, and to this was added a saturated aqueous solution of sodium iodide in water until no further precipitation occurred. After standing for a week, the clear liquor was poured off and the mixture of tar and crystalline matter that had separated was triturated with a little cold absolute alcohol, which dissolved the tar and left a small quantity of akuammine hydriodide. The alcoholic washings were added to the mother-liquors, and the whole was fractionally precipitated with sodium carbonate solution, the first few drops of precipitant serving to remove a dark brown, sticky base, from which a clear pale yellow mother-liquor was poured off. This on further addition of sodium carbonate solution yielded the crude alkaloid (B) as a pale yellow powder, m. p. 104° (air-dry) or 167° (dried in a vacuum).

The seeds received from the Imperial Institute consisted of several samples collected at different times, and from one of these, on recrystallisation of the crude akuammine sulphate as described above, the first fraction consisted of the well-crystallised sulphate of alkaloid (D) (p. 1958). As only 2 g. of this alkaloid have been obtained, it has been considered advisable to conserve it for the present and only to make such observations upon it as would not entail the loss of material. It is therefore only possible to put its chief characteristics on record.

The quantity of alkaloids present in *P. Klaineana* seeds is more than 5%, but the exact amount cannot be determined by any of the ordinary methods of estimation, because the alkaloids cannot

be precipitated completely from solution in acids by alkalis, nor can the alkaloid left in such alkaline filtrate be completely removed by any of the ordinary immiscible solvents. The yield of crude akuammine is about 0·6%. The four alkaloids are readily differentiated by their physical properties and colour reactions. Alkaloid A is insoluble in all ordinary solvents except acids and alkalis, and from these it is precipitated on dilution with water. Alkaloid B is readily soluble in all ordinary solvents except water, and solutions of its salts, unlike those of any of the other three, give an intense indigo-blue colour with ferric chloride. Akuammine (alkaloid C) dissolves in concentrated sulphuric acid without coloration, but gives an intense blood-red colour, stable for several days, with nitric acid. The second crystalline alkaloid (D) gives no colour with sulphuric acid but a vivid green, fading to yellow in a few hours, with nitric acid.

In the following descriptions, the " melting points " are corrected; in each case, except for akuammine hydrate, they are points at which the substance froths up the tube. The temperature at which this occurs varies with the rate of heating, *e.g.*, pure akuammine hydrochloride can be made to melt and decompose at any temperature from 215° to 227°. The melting points recorded for the base and its salts were taken alongside the pure hydrochloride, melting at 227°, so that they are comparable among themselves. The optical rotations are for the dried substance in each case.

Akuammine (Alkaloid C).

The base is prepared by adding excess of sodium carbonate solution to a warm, aqueous solution of a purified salt. It is sparingly soluble in cold alcohol, but once dissolved in boiling alcohol it crystallises from the latter only by spontaneous evaporation in minute, colourless needles, m. p. 255°, $[\alpha]_D^{20°}$ −66·7° (in alcohol; $c = 0·504$) or −73·4° (in chloroform; $c = 0·8716$). It is rather more soluble in chloroform and sparingly soluble in acetone or ether (Found : C, 69·0, 69·1; H, 7·2, 7·0; N, 7·5. $C_{22}H_{28}O_4N_2$ requires C, 68·7; H, 7·3; N, 7·3%).

Akuammine hydrobromide, prepared like the sulphate (see above), separates from dilute hot aqueous or alcoholic solutions in faintly grey, long, slender prisms, or from concentrated solutions in the same solvents in small needles, m. p. 228°, $[\alpha]_D^{20°}$ −26·05° (in water; $c = 0·6076$). The air-dry salt loses in a vacuous desiccator 3·61% and no further loss takes place in a vacuum at 100°. (Calc. for $C_{22}H_{28}O_4N_2,HBr,H_2O$: H_2O, 3·7%. Found for dry salt : C, 56·1, 56·3; H, 6·0, 6·1; Br, 16·6. $C_{22}H_{28}O_4N_2,HBr$ requires C, 56·7; H, 6·3; Br, 17·1%). The *hydrochloride* closely resembles the

hydrobromide in appearance, but is of paler colour and rather more soluble in water or alcohol. It has m. p. 227° and $[\alpha]_D^{22°}$ −26·6° (in water; $c = 0{\cdot}8769$) or −32·8° (in alcohol; $c = 1{\cdot}716$) and crystallises with one molecule of water (Found: loss in a vacuum at 120°, 4·0. $C_{22}H_{28}O_4N_2,HCl,H_2O$ requires H_2O, 4·1%. Found for dry salt: C, 62·5, 62·6; H, 6·9, 6·7; N, 7·1; Cl, 8·5, 8·4. $C_{22}H_{28}O_4N_2,HCl$ requires C, 62·7; H, 7·0; N, 6·6; Cl, 8·4%). The *sulphate*, prepared as described above, crystallises from hot water or hot alcohol in rosettes of flattened needles, which rapidly become red on exposure to light. It melts at 221° and has $[\alpha]_D^{19°}$ −40·3° (in water; $c = 2{\cdot}0868$). The salt is abnormal in composition, crystallises with 10 molecules of water of crystallisation, of which 9 are lost at atmospheric temperature in a vacuous desiccator over calcium chloride. Loss (*a*) from air-dry salt at 100° in a vacuum, 11·5; (*b*) from salt previously dried to constant weight in a vacuous desiccator, 1·8. $(C_{22}H_{28}O_4N_2)_3,2H_2SO_4$, for $10H_2O$, requires H_2O 11·8%, and for $1H_2O$ 1·3% [Found for dry salt: C, 58·8; H, 6·7; S, 4·45. $(C_{22}H_{28}O_4N_2)_3,2H_2SO_4$ requires C, 58·7; H, 6·5; S, 4·7%]. This may be a double compound consisting of one molecule of the acid salt with one molecule of the normal salt (B,H_2SO_4; B_2,H_2SO_4). In this connexion, it may be noted that another dibasic acid, *viz.*, oxalic acid, yields at least three salts, which, however, have not been satisfactorily separated.

The *hydriodide* is precipitated as a crystalline powder on adding potassium iodide to even a dilute solution in water of any soluble salt of akuammine. It cannot be crystallised from hot water without decomposition, but separates from hot alcohol in anhydrous, minute, pale grey needles, m. p. 226° (Found: C, 52·0; H, 6·0. $C_{22}H_{28}O_4N_2,HI$ requires C, 51·5; H, 5·7%).

The *nitrate*, also prepared by precipitation, crystallises from boiling alcohol in pale cream-coloured needles, m. p. 224°. The *thiocyanate*, similarly prepared, crystallises from alcohol in pale greyish needles, m. p. 218°. The *perchlorate*, precipitated by addition of sodium perchlorate to a solution of the hydrochloride in water, crystallises from hot alcohol in colourless, spheroidal granules, m. p. 215°, if the solution is concentrated, and from more dilute solutions in colourless needles also melting at 215°. This salt becomes pink on exposure to air and resinous after several crystallisations from boiling alcohol. The *picrate* crystallises from hot alcohol in rosettes of brilliant yellow needles, m. p. 199°. The *picrolonate*, precipitated in minute, yellow needles, darkens at 160° and froths at 194°. On dissolution in hot alcohol it deposits a deep blue dye.

No chloroaurate has been prepared, as akuammine hydrochloride

reduces gold chloride immediately. It also reduces platinic chloride and silver nitrate in the cold and Fehling's solution on warming.

Methoxyl and methylimino-groups. Determinations of these groups were made on the base and the hydrochloride (Found for base: MeO, 8·87; NMe, 8·2. Calc. for MeO, 8·0 and for NMe, 7·5%. Found for hydrochloride: MeO, 7·73; NMe, 6·6. Calc. for MeO, 7·4 and for NMe, 6·9%).

Akuammine hydrochloride gives (1) a rose-red colour with vanillin or piperonal in presence of hydrochloric acid, (2) a yellowish-brown colour with dimethylaminobenzaldehyde (Ehrlich's reagent), changing on long standing to red with a green fluorescence, (3) with bromine water a pink colour, the solution becoming cloudy on further addition of bromine.

Action of methyl iodide on akuammine. The pure base does not dissolve in methyl iodide, but when suspended in the reagent the latter gradually contracts in volume and in about 2 days conversion into a *monomethiodide* appears to be complete. This separates from solutions in hot methyl alcohol in rosettes of colourless prisms, m. p. 274°. On melting, the substance froths vigorously and gives off a vapour with a fishy odour, probably due to dimethylamine. The methiodide in solution gives no precipitate with alkali hydroxides or carbonates and is therefore the iodide of a quaternary base (Found: C, 52·7; H, 5·7; I, 24·4; MeO, 6·8; NMe, 9·7. $C_{22}H_{28}O_4N_2,CH_3I$ requires C, 52·4; H, 5·9; I, 24·1; MeO, 5·9; 2NMe, 11·1%). The results for methoxyl are high and those for methylimino-groups low. In carrying out these estimations, it was noticed that elimination of methyl iodide in the second stage (methylimino-determination) began at the low temperature of 180°, immediately after addition of ammonium iodide, so that it appears likely that part of the methyl iodide collected in the earlier stage (methoxyl determination) is really due to methylimino-groups. The total amount of methyl iodide formed in the estimation, calculated from the amount of silver iodide weighed, was 79·07%, whilst there should be formed, assuming the presence of one methoxyl and two methylimino-groups, 80·9%. Cases in which there is no sharp distinction between the conversion of methoxyl and methylimino-groups into methyl iodide in such estimations have been observed previously, *e.g.*, in ergotoxine (Barger and Ewins, J., 1918, **113**, 235; a summary of literature on this subject is given on page 237).

Action of methyl iodide and alkali on akuammine. Akuammine base (1 g.) was dissolved in *N*-sodium methoxide solution in methyl alcohol (2·7 c.c.), and methyl iodide (4 c.c.) was added. This mixture, after standing for 4 days, was boiled for 4 hours. The liquid was taken to dryness under reduced pressure, and the residue

dissolved in boiling water, from which it separated on cooling as a colourless oil. The solution in water gives a precipitate of a new oily base on addition of sodium carbonate or alkali hydroxide. Neither the base nor any of its salts, except the picrate, have so far been induced to crystallise. The *picrate* is precipitated on adding picric acid in methyl alcohol to a solution of the base or the hydriodide in the same solvent, and can be crystallised either from boiling water or from methyl alcohol, producing in the former case canary-yellow needles or rosettes of needles and in the latter bronze-tinted, dense rosettes of prisms, both forms melting at 205° (Found : MeO, 10·0; NMe, 6·0. $C_{22}H_{29}O_5N_2{\cdot}CH_3,C_6H_3O_7N_3$ requires 2MeO, 9·6; NMe, 4·5%). These results agree with the assumption that in this reaction the akuammine is first hydrated by the alkali (see below) and that the hydrate undergoes *O*-methylation either on the hydroxyl group originally present in akuammine or on a new group formed in the hydration.

Acetylation of akuammine. The pure base (3·8 g.) was boiled for 5 minutes with acetic anhydride (10 c.c.), the solution left to cool, and the excess of reagent removed by distillation under reduced pressure. The residue was dissolved in water, the liquid poured into sodium carbonate solution, and the precipitate collected, sucked dry on the filter, and dissolved in the minimum quantity of boiling alcohol, from which it separated on cooling in rosettes of colourless prisms (yield, 2·4 g.), m. p. 226°. The melting point was not changed by recrystallisation. The concentrated mother-liquors, which had ceased to deposit crystals, were taken to dryness, the residue was dissolved in four times its weight of boiling *N*/2-hydrobromic acid, and the solution filtered hot. On cooling, it deposited a silky mass of hair-like needles, m. p. 236°, of *acetylakuammine hydrobromide* (yield, 1·1 g.), the melting point of which remained unchanged on recrystallisation. This hydrobromide on solution in boiling water and precipitation with sodium carbonate solution furnished the pure *base*, m. p. 226°. From the mother-liquors of the hydrobromide the rest of the acetylated base was precipitated as the *picrate* (0·5 g.), which crystallised with difficulty from concentrated solutions in methyl alcohol, in gelatinous masses of rosettes of minute, yellow needles, m. p. 168° after drying in air. The acetylated base becomes pink on exposure to air and has $[\alpha]_D^{20°}$ −52·08° ($c = 0{\cdot}64$ in alcohol) (Found for the base : C, 67·5, 67·45; H, 6·9, 6·7; MeO, 9·3; NMe, 6·9; acetic acid formed on alkaline hydrolysis, 13·1. $C_{22}H_{27}O_4N_2{\cdot}CO{\cdot}CH_3$ requires C, 67·6; H, 7·1; MeO, 7·3; NMe, 6·8; acetic acid, 14·1%. Found for hydrobromide : C, 57·3, 57·1; H, 5·9, 6·0; Br, 15·95. $C_{22}H_{27}O_4N_2{\cdot}CO{\cdot}CH_3,HBr$ requires C, 56·8; H, 6·2; Br, 15·75%).

The base recovered from the acetic acid estimation appeared to be akuammine hydrate, m. p. above 300° (see below).

Action of alkalis on akuammine. Akuammine dissolves slowly in solutions of ammonia or alkali hydroxides, forming in the course of a few days dark brown liquids, which on neutralisation by acids deposit precipitates of a mixture of bases. For the examination of these products it has been found most convenient to treat akuammine with a known quantity of a normal solution of sodium ethoxide in alcohol, in which it dissolves immediately, keep the solution for several days, remove the alcohol, and treat the residue with water; the sodium derivatives presumably first formed and stable in alcohol are then almost completely dissociated, leaving a dark brown precipitate. The latter on digestion first with alcohol and then with chloroform is obtained as a nearly colourless powder, which does not sinter up to 300° and after heating to this temperature can usually be shaken out of the melting point tube as an orange-brown powder. The product is insoluble in all ordinary solvents, and is finally purified by dissolving it in a known quantity of sodium ethoxide in alcohol, adding sufficient alcohol to dilute the solution to a concentration of about 1 part in 5 parts, and then neutralising the filtered liquid with the calculated quantity of *N*/2-acetic acid; after a few minutes, practically the whole of the product crystallises in small, spheroidal granules of minute needles, which do not sinter or melt up to 310°. It dissolves immediately in solutions of ammonia or alkali hydroxides, but such solutions gelatinise when carbon dioxide is passed into them: the jelly can be filtered out and dries up to a brown powder having the characters of the original substance. The product appears to be an *akuammine hydrate* formed by addition of a molecule of water to akuammine (Found: C, 65·0, 65·1; H, 6·9, 6·8. $C_{22}H_{28}O_4N_2,H_2O$ requires C, 65·6; H, 7·5%). The yield in the above process has varied from 15 to 41% of the akuammine used. The by-products soluble in alcohol and chloroform are brown, amorphous substances soluble in alkalis, but they also form salts, *e.g.*, hydrobromides, which are sparingly soluble in cold water or saline aqueous solutions but very readily soluble in alcohol, acetone, or chloroform.

Base D.

The akuamma seeds used for this work consisted of a number of samples and from one of these the crude alkaloidal sulphates, prepared as described on p. 1953, on recrystallisation from water gave a fraction crystallising in colourless, transparent, flattened cubes. This *sulphate*, m. p. 161°, $[\alpha]_D^{17°}$ −594·1° (c = 0·4226 in water) or −539·8° (c = 0·2860 in water), contains 8·9% of water

of crystallisation, of which 2·4% is lost in a vacuous desiccator at atmospheric temperature. The *base*, obtained by adding sodium carbonate solution to an aqueous solution of the sulphate, crystallises from hot alcohol in brilliant, colourless leaflets, m. p. 177·5°, $[\alpha]_D^{19°}$ −737·5° (c = 0·4932 in alcohol), −737·7° (c = 0·3504 in chloroform). The *nitrate* forms colourless needles, m. p. 180—181°. The *picrate* can be crystallised by dissolving it in boiling chloroform and adding an equal volume of boiling alcohol. From this mixture on cooling, it separates in dull yellow needles, m. p. 169°.

Base D gives a grass-green coloration when a mere trace is added to a drop of concentrated nitric acid. Like akuammine, it gives colours with aromatic aldehydes in presence of hydrochloric acid, *viz.*, indigo-blue with vanillin and magenta with piperonal, both changing to bright ultramarine-blue after a few days and remaining stable for at least 14 days. The alkaloid gives no coloration with Gaebel's test for methylenedioxy-groups.

The authors are indebted to the late Mr. S. E. Pusey and to Messrs. L. Barnett and H. C. Clarke for much assistance in the extraction of the alkaloids and in the analyses of the various preparations described.

WELLCOME CHEMICAL RESEARCH LABORATORIES.

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CCLV.—*The Isomerism of the Oximes. Part XXXI. The Furfuraldoximes and 2-Methoxy- and 4-Methoxy-1-naphthaldoximes.*

By OSCAR LISLE BRADY and RICHARD FRANK GOLDSTEIN.

THE greater part of the study of the aldoximes from the point of view of stereoisomerism has been devoted to those in which the aldoximino-group is attached to the benzene ring. The stability of the α-isomeride in the benzaldoximes, in contrast with the aliphatic aldoximes where the β-form is the normal product, makes it of some interest to consider the effect of other ring systems on the relative stability of the two isomerides. The case of furfuraldoxime is of historic importance, since this was the first aldoxime to be obtained in two forms (Odernheimer, *Ber.*, 1883, **16**, 2988). Goldschmidt and Zanoli (*Ber.*, 1892, **25**, 2573) also prepared the two isomerides and determined their configuration, but thought they found indications of abnormal behaviour, since in the acetylation of the α-oxime and subsequent hydrolysis some furfuronitrile and a mixture of the two oximes were obtained. Similarly, Minunni

(*Gazzetta*, 1896, **26**, i, 463) obtained a mixture of oximes on hydrolysis of benzoyl-α-furfuraldoxime.

This work has now been repeated and the origin of the difficulties of previous workers traced to the fact that the α-oxime in the presence of hot solvents is partly converted into the β-isomeride, a phenomenon never observed in the benzaldoximes. With care, a crystalline acetyl-α-furfuraldoxime can be prepared; this on hydrolysis gives nearly pure α-furfuraldoxime, which can also be obtained by hydrolysis of the benzoyl compound and isolation of the oxime by special means. β-Furfuraldoxime is obtainable under conditions which will not give β-benzaldoxime, being much more stable than that compound. The furfuraldoximes accordingly occupy an intermediate position between the benzaldoximes and the aliphatic aldoximes.

No oximes of the naphthalene series have been investigated from the point of view of the stereochemical hypothesis, so 2-methoxy-1-naphthaldoxime and 4-methoxy-1-naphthaldoxime have now been studied. The products of oximation have the α-aldoxime structure and we have been unable to convert either into the β-isomeride. As they may both be regarded as *o*-substituted benzaldoximes, this was not unexpected. On methylation of 2-methoxy-1-naphthaldoxime, a mixture of *N*- and *O*-ethers was obtained, the former predominating; 4-methoxy-1-naphthaldoxime gave a mixture of about equal amounts of *N*- and *O*-ethers. Both oximes therefore differ markedly from the α-benzaldoximes in the relative amounts of *N*- and *O*-ethers produced on methylation.

Experimental.

α-Furfuraldoxime.—Furfuraldehyde (13·5 g.) was added slowly to a cold mixture of sodium hydroxide (14 g. in 15 c.c of water) and hydroxylamine hydrochloride (12 g. in 30 c.c. of water). After 1 hour, the solution was filtered and cooled in a freezing mixture and a slight excess of an ice-cold, saturated aqueous solution of ammonium chloride was slowly added with stirring. The crystalline precipitate was washed with a little ice-cold water and air-dried. The yield of crude oxime (m. p. 51—64°) was 11·5 g. After crystallising three times from benzene and light petroleum, 4 g. of pure α-oxime were obtained, m. p. 75—76° (Goldschmidt and Zanoli, *loc. cit.*, give 73°). The details must be carefully followed, otherwise an inseparable mixture of the two isomerides may be obtained. In one experiment, a crude oxime, m. p. 42—45°, was obtained and repeated crystallisations failed to raise the melting point above 48—52°. It is probable that the material (m. p. 49—56°) obtained by Odernheimer (*loc. cit.*) was a similar mixture. When the pure

α-oxime (0·5 g.) was boiled with benzene (20 c.c.) under reflux for 4 hours and the solvent evaporated, a product, m. p. 47—48°, was obtained which was apparently a mixture of the α- and β-isomerides, since the addition of either raised its melting point.

Acetyl-α-furfuraldoxime.—α-Furfuraldoxime (2·5 g.) was slowly added to acetic anhydride (12 c.c.), and warmed to 30°; it then dissolved. On decomposing the excess of anhydride with 2*N*-sodium carbonate, crystals separated which were collected, air-dried, and dissolved in warm light petroleum; on cooling the solution to — 20° or — 40°, *acetyl-α-furfuraldoxime* separated in colourless prisms, m. p. 34—35° (Found: N, 9·4. $C_7H_7O_3N$ requires N, 9·2%). The acetyl derivative was warmed with 2*N*-sodium hydroxide until it dissolved; there was no odour of furfuronitrile. On cooling the solution, adding saturated ammonium chloride solution, extracting the mixture twice with ether, and evaporating the solvent with a current of air, an oxime was obtained which, after being pressed on a porous tile, melted at 69—72° and was nearly pure α-oxime. Goldschmidt and Zanoli (*loc. cit.*) obtained on acetylation an oil which on hydrolysis gave some furfuronitrile and an oxime, m. p. 49—60°.

Benzoyl-α-furfuraldoxime.—Crude α-furfuraldoxime, m. p. 51—57° (7 g.) was slowly added with cooling to benzoyl chloride (30 g.) and the product was poured into 2*N*-sodium hydroxide (250 c.c.), vigorously shaken for 30 minutes, and kept for 12 hours. The benzoyl derivative which separated was crystallised three times from alcohol; it then melted at 138—139° (compare Minunni, *loc. cit.*). The benzoyl derivative (5 g.) was heated with 2*N*-sodium hydroxide (50 c.c.), and the solution was cooled, saturated with carbon dioxide, and extracted with ether; removal of the solvent by a current of air gave a nearly pure α-oxime, m. p. 68—73°. It is essential that the solutions of the α-oxime should not be warmed, otherwise partial conversion into the β-oxime occurs.

β-*Furfuraldoxime.*—Hydroxylamine hydrochloride (10 g.) in methyl alcohol (40 c.c.) was treated with crystallised sodium acetate (19·5 g.) in dilute alcohol (40 c.c.), and furfuraldehyde (12 g.) added. The mixture was kept for 24 hours, the precipitated sodium chloride removed, and the solution evaporated in a vacuum at room temperature to about 30 c.c. and then poured into water (70 c.c.). The precipitated β-oxime (m. p. 89—91°) was crystallised three times from 10% alcohol with the addition of a little animal charcoal; a nearly quantitative yield was then obtained of the pure β-oxime, m. p. 91—92° (Goldschmidt and Zanoli give 89°). The β-oxime (2·5 g.) was dissolved in acetic anhydride (10 c.c.) at 30° and poured into 2*N*-sodium carbonate. When all the anhydride was decom-

posed, the oil was extracted with ether and hydrolysed, after removal of the solvent, by boiling it with 40% potassium hydroxide solution. Ammonia was evolved and extraction of the acidified solution with ether yielded pyromucic acid, identified by its reactions and by comparison with an authentic specimen.

α-2-*Methoxy*-1-*naphthaldoxime*.—To a mixture of hydroxylamine hydrochloride (7·5 g.) and sodium hydroxide (10 g.) in water (110 c.c.) was added a solution of 2-methoxy-1-naphthaldehyde (14 g.) in hot alcohol (20 c.c). The sodium salt of the oxime (which is very sparingly soluble in water) separated as a mass of crystals; after 1 hour, the oxime was liberated by addition of excess of a saturated solution of ammonium chloride, filtered off, washed, and dried (yield, almost quantitative). After three crystallisations from hot benzene, α-2-*methoxy*-1-*naphthaldoxime* formed white plates, m. p. 154—155° (Found: N, 7·3. $C_{12}H_{11}O_2N$ requires N, 7·0%).

α-*Acetyl*-2-*methoxy*-1-*naphthaldoxime*, prepared in the usual way, and crystallised from alcohol, formed white needles, m. p. 79—80° (Found: N, 5·9. $C_{14}H_{13}O_3N$ requires N, 5·8%). On hydrolysis with hot 2*N*-sodium hydroxide, the needles of the acetyl derivative are gradually replaced by the plates of the sodium salt of the oxime. On addition of ammonium chloride, the α-oxime was recovered unchanged.

α-2-*Methoxy*-1-*naphthaldoxime Hydrochloride*.—The oxime (2 g.) was dissolved in boiling chloroform (75 c.c.), and dry hydrogen chloride passed in for 20 minutes. The precipitated *hydrochloride* was collected, washed with chloroform, and pressed on a porous tile. It formed a bright yellow powder, m. p. 145—147° (decomp.) (Found: Cl, 16·4. $C_{12}H_{11}O_2N,HCl$ requires Cl, 14·9%). With sodium hydroxide and ammonium chloride, the hydrochloride regenerated the α-oxime; no inversion had taken place.

Methylation of α-2-*Methoxy*-1-*naphthaldoxime*.—The oxime (7·0 g.), dissolved in hot alcohol (85 c.c.), was treated with sodium ethoxide (1·05 g. of sodium in 25 c.c. of alcohol), and methyl iodide (5 g.) added. The solution was boiled under reflux for 30 minutes and kept for 12 hours, the alcohol allowed to evaporate somewhat, and excess of water added. An emulsion was formed, which was extracted first with ether, then with chloroform. The ethereal extract on evaporation gave a thick oil (2·4 g.) which solidified when cooled, yielding a hard, brown solid, m. p. 51—54°, consisting mainly of *O*-ether, but also containing a little *N*-ether, unchanged oxime, and other impurities. The *O*-ether is best separated by prolonged distillation in steam, in which it is difficultly volatile; it was identified in the distillate by comparison with an authentic specimen obtained by synthesis.

The chloroform extract gave a solid (4·6 g.), m. p. 106—107°. After some weeks, the m. p. had fallen to 83—87°. This compound on crystallisation from benzene gave pure *N-methyl-2-methoxy-1-naphthaldoxime hydrate*, fine needles, m. p. 88—89° (Found: N, 6·0; H_2O, 7·6. $C_{13}H_{13}O_2N,H_2O$ requires N, 6·0; H_2O, 7·7%). The anhydrous *N-methyl-2-methoxy-1-naphthaldoxime*, obtained by desiccation of the hydrate in a vacuum over calcium chloride, formed stout prisms, m. p. 118—119°, which hydrate readily (Found: N, 6·5. $C_{13}H_{13}O_2N$ requires N, 6·5%). Both the hydrated and the anhydrous ether yield *N*-methylhydroxylamine and 2-methoxy-1-naphthaldehyde on gentle boiling with acids.

α-O-*Methyl-2-methoxy-1-naphthaldoxime*.—2-Methoxy-1-naphthaldehyde (3·5 g.) and *O*-methylhydroxylamine (0·95 g.) were dissolved in alcohol (30 c.c.) and kept for 12 hours. The alcohol was allowed to evaporate spontaneously, and the dark solid residue purified by steam distillation and crystallisation from alcohol. α-O-*Methyl-2-methoxy-1-naphthaldoxime* formed colourless, short prisms, m. p. 65° (Found: N, 6·8. $C_{13}H_{13}O_2N$ requires N, 6·5%).

4-*Methoxy*-1-*naphthaldehyde*.—4-Hydroxy-1-naphthaldehyde (24 g.) was heated with potassium hydroxide (8 g. in 35 c.c. of water), and methyl sulphate (13 c.c.) added slowly with shaking. The mixture was heated on the water-bath for 30 minutes, potassium hydroxide (5·5 g. in 20 c.c. of water) and methyl sulphate (8 c.c.) were then added alternately in small quantities with shaking. Heating was continued for 30 minutes, and the solution was cooled and extracted with ether. The aqueous portion on acidification gave 4·8 g. of impure 4-hydroxy-1-naphthaldehyde. The ethereal portion was well washed with dilute sodium hydroxide solution, then with water, dried, and evaporated. The yield of crude methoxyaldehyde, which was sufficiently pure for the next operation, was 10·8 g. A considerable quantity of tar was formed. 4-Methoxy-1-naphthaldehyde has previously been prepared by boiling 4-hydroxy-1-naphthaldehyde with methyl iodide and potassium hydroxide in alcoholic solution (Gattermann, *Annalen*, 1907, **357**, 365).

α-4-*Methoxy-1-naphthaldoxime*, prepared from the crude aldehyde in a similar way to the 2-methoxy-compound, crystallised from benzene in white needles, m. p. 107—108° (Found: N, 7·3. $C_{12}H_{11}O_2N$ requires N, 7·0%).

α-*Acetyl-4-methoxy-1-naphthaldoxime*, prepared in the usual way, crystallised from alcohol in colourless needles, m. p. 102° (Found: N, 5·8. $C_{14}H_{13}O_3N$ requires N, 5·8%). On warming it with 2*N*-sodium hydroxide and saturating the solution with carbon dioxide, the original α-oxime was obtained.

α-4-*Methoxy-1-naphthaldoxime hydrochloride*, prepared in the

same way as the corresponding 2-methoxy-compound, formed a yellowish-green powder, m. p. 144—145° (decomp.) (Found: Cl, 15·1. $C_{12}H_{11}O_2N,HCl$ requires Cl, 14·9%). On decomposing it with 2*N*-sodium carbonate, the original oxime was regenerated.

Methylation of α-4-*Methoxy*-1-*naphthaldoxime*.—The oxime (6·55 g. in 59 c.c. of alcohol), sodium (0·8 g. in 20 c.c. of alcohol), and methyl iodide (5·1 g. in 20 c.c. of alcohol) were boiled under reflux for 20 minutes and kept for 12 hours. The methylated product was worked up in the same way as the 2-methoxy-oxime, there being obtained 3·1 g. of *O*-methyl ether and 3·0 g. of *N*-methyl ether. α-O-*Methyl*-4-*methoxy*-1-*naphthaldoxime* formed colourless needles, m. p. 38—39°, from alcohol and water (Found: N, 6·5. $C_{13}H_{13}O_2N$ requires N, 6·5%). α-N-*Methyl*-4-*methoxy*-1-*naphthaldoxime* is dimorphic and separated from hot benzene in yellow prisms, m. p. 158—159° (Found: N, 6·4%), which changed to dark grey plates on keeping in contact with the mother-liquor for 2 hours. The grey modification passed back into the yellow on crystallisation or on heating at 100° for some time.

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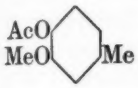
CCLVI.—*Nitro-derivatives of the Homopyrocatechol Ethers.*

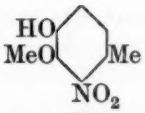
By ALBERT EDWARD OXFORD.

IT has previously been shown (Oxford, J., 1926, 2004) that the action of acetyl nitrate on *o*-methoxyphenyl acetate at −15° gives rise to 3-nitro- and 5-nitro-2-methoxyphenyl acetates in about equal quantities. It was hoped that the application of this method to *m*-methoxy-*p*-tolyl acetate (I) would yield a relatively considerable proportion of the 2-nitro-derivative and provide a new and more direct route to 2-nitrohomoveratrole, although it was, of course, recognised that the effect of the methyl group would be to suppress substitution in the position between it and the methoxyl group (compare the nitration of aceto-*m*-toluidide, Cohen and Dakin, J., 1903, **83**, 331; and of *m*-cresol, Gibson, J., 1923, **123**, 1269). In point of fact, the effect was such that the yield of the 2-nitro-derivative could not be raised above 5%, although nearly every possible variation in the experimental conditions was tried, including a nitration at − 40°. The method did, however, provide a means of preparing the hitherto unknown nitro-derivatives of creosol and homoveratrole, *viz.*, 2-*nitrocreosol* (II), 2 : 5-*dinitrocreosol* (III)

(readily obtained by nitrating II in acetic acid solution), and 2 : 5-*dinitrohomoveratrole* (IV).



(I.)



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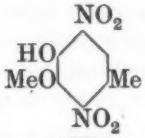

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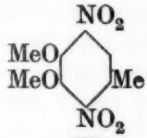
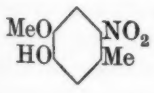


(IV.)

In view of the interest attaching to 2-nitrohomoveratrole (see Oberlin, *Arch. Pharm.*, 1925, **263**, 641; Gulland and Robinson, J., 1926, 1976; compare also Dadswell and Kenner, this vol., p. 580), and of the strong probability that, like homoveratrole and 2-nitro-*m*-tolyl methyl ether, it should be a solid at the ordinary temperature, a method for its complete separation from 6-nitrohomoveratrole was much needed. It was found that under conditions of alkaline hydrolysis which leave the 2-nitro-isomeride unaffected, 6-nitrohomoveratrole is quantitatively demethylated to 6-nitro*iso*creosol (V), and a specimen of 2-nitrohomoveratrole prepared from 2 : 6-dinitrohomoveratrole according to Oberlin's details, after being submitted to this treatment, was found to contain only a trace of 6-nitrohomoveratrole. The purified 2-nitrohomoveratrole could then for the first time be obtained crystalline, having m. p. 6—7·5°. Apparently sodium sulphide (the reducing agent used by Gulland and Robinson, whose final product was undoubtedly a mixture of the two nitrohomoveratroles) attacks both nitro-groups in 2 : 6-dinitrohomoveratrole, whilst ammonium sulphide (the reducing agent used by Oberlin), being milder and more specific in its action, reduces only the 6-nitro-group.

In conclusion, some comparative experiments have been carried out in the *o*-creosol series. The nitration of *o*-homoveratrole by concentrated nitric acid yields only the 5-nitro-derivative (VI) (Cain and Simonsen, J., 1914, **105**, 156; Majima and Okazaki, *Ber.*, 1916, **49**, 1482), and the same result is obtained if acetyl



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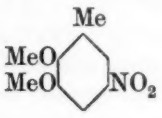

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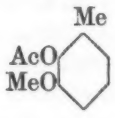

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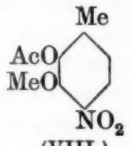


(VIII.)

nitrate at −15° is the nitrating agent. The nitration of 3-methoxy-*o*-tolyl acetate (VII) under conditions which convert *o*-methoxyphenyl acetate into its 5-nitro-derivative only, yields chiefly the 4-nitro-derivative (VIII) and not, as might be expected, the 6-nitro-derivative.

Experimental.

Nitration of m-*Methoxy*-p-*tolyl Acetate* (I).—A mechanically stirred solution of the acetate (32·2 g.) and redistilled acetyl chloride (35 c.c.) in pure dry carbon tetrachloride (140 c.c.), cooled in a freezing mixture and protected from moisture, was treated during 2½ hours with dry, very finely powdered silver nitrate (36 g.). The 6-nitro-derivative began to crystallise just before all the silver nitrate had been added. Stirring was continued for a further hour, the reaction mixture filtered, and the precipitate—which contained the greater part of the 6-nitro-derivative mixed with silver salts—washed with carbon tetrachloride. The deep red filtrate was shaken twice with water, dried over anhydrous sodium sulphate, and, after evaporation of the solvent, distilled in a vacuum, three fractions being collected : (i) (Up to 167°/13 mm.) 5 g. of a red liquid; (ii) (167—177°/13 mm.) 8 g., mostly liquid; (iii) (177—210°/13 mm.) 5 g. of a solid (6-nitro-3-methoxy-*p*-tolyl acetate); (i) and the liquid part of (ii) were combined and hydrolysed by warming on the steam-bath with 2*N*-sodium hydroxide.

6(?)-*Chlorocreosol*.—The crude phenolic mixture was steam-distilled; the brown, semi-solid material (about 4 g.) that came over, after repeated crystallisation from water, was obtained in colourless, glistening, rectangular leaflets, m. p. 71° (Found : Cl, 19·7; *M*, in camphor, 174. $C_8H_9O_2Cl$ requires Cl, 20·5%; *M*, 172). It is sparingly soluble in cold water and dissolves readily in all organic solvents with the exception of light petroleum. It has a faint, guaiacol odour, gives no coloration with ferric chloride, and does not dissolve chemically in sodium bicarbonate solution.

Its *acetyl* derivative crystallises from light petroleum in colourless, thick tablets, m. p. 61° [Found : MeO (micro-Zeisel), 14·2. $C_{10}H_{11}O_3Cl$ requires MeO, 14·5%]. It is readily soluble in ethyl and methyl alcohols and moderately easily soluble in hot water.

The *methyl ether*, obtained by the xylene–methyl sulphate–potassium carbonate method, crystallises from aqueous alcohol in colourless, shining leaflets, m. p. 37—38°. It has an almost ethereal odour recalling that of *m*-methoxy-*p*-tolyl acetate, and gives a yellow coloration with concentrated sulphuric acid. In order to decide which position (2 or 6) is occupied by the chlorine atom, the behaviour of this ether on nitration was investigated. It dissolved in concentrated nitric acid to a red solution, from which nothing was precipitated by addition of water at the end of 10 minutes, but when nitrated in acetic anhydride solution at 0°, by concentrated nitric acid, it yielded a minute amount of a brown solid which crystallised from light petroleum in colourless, well-defined prisms, m. p. 89°. The amount of this substance obtained

was insufficient for further investigation, but the behaviour of the chlorocreosol towards nitrating agents recalls that of 6-nitrohomoveratrole and is quite unlike that of 2-nitrohomoveratrole, which is readily nitrated to 2 : 6-dinitrohomoveratrole.

2-*Nitrocreosol* (II).—The nitrocreosols remaining in the distillation flask after the removal of chlorocreosol * were extracted with ether, and after evaporation of the solvent a dark oil remained, the solution of which in boiling light petroleum (b. p. 60—80°) deposited, on cooling, 6-nitrocreosol mixed with a little tar. After evaporation of the mother-liquor, a yellow oil remained (1·5 g.) which proved to be fairly pure 2-nitrocreosol. It was again heated with a little light petroleum, and the undissolved oil (1 g.), which would not crystallise at — 15°, was used in the experiments described below.

2-*Nitro*-3-*methoxy*-4-p-*nitrobenzyloxytoluene*.—The benzoyl derivative of 2-nitrocreosol was an uncrystallisable oil, and the phenol had to be characterised by the preparation of its p-*nitrobenzyl ether*. 2-Nitrocreosol (1·6 g., a slight excess) together with *p*-nitrobenzyl bromide (1·83 g.) was dissolved in a solution of sodium (0·19 g.) in absolute alcohol (60 c.c.), and the whole boiled under reflux for 3½ hours; much water was then added. The precipitate (m. p. 100°) obtained, after five crystallisations from alcohol, separated in fern-like aggregates of minute, colourless, flat rods, m. p. 114—114·5°, unaltered by further crystallisations from alcohol or light petroleum (Found : N, 9·1, 8·9. $C_{15}H_{14}O_6N_2$ requires N, 8·8%). It is readily soluble in most organic solvents.

6-*Nitro*-3-*methoxy*-4-p-*nitrobenzyloxytoluene* was prepared from 6-nitrocreosol by an exactly similar method. It was crystallised from hot alcohol, in which it was very sparingly soluble, and then from benzene, separating in pale yellow, feathery needles, m. p. 202—203° (Found : C, 56·1; H, 4·8. $C_{15}H_{14}O_6N_2$ requires C, 56·6; H, 4·4%).

2 : 5-*Dinitrocreosol* (III).—2-Nitrocreosol (2·6 g.) dissolved in glacial acetic acid (9 c.c.) was nitrated by the addition of a solution of nitric acid (*d* 1·42; 3·5 c.c.) in glacial acetic acid (3 c.c.) with constant stirring and cooling in ice-water, the first half of this solution being added during 10 minutes and the rest during 1 minute. Water was added immediately and the product was collected, washed, and dried (yield, 0·67 g., *i.e.*, 25% of the theoretical). It separated from light petroleum (b. p. 40—60°) in yellow leaflets, m. p. 86—87°, not altered by a second crystallisation from that solvent, from which it was also deposited in flat needles

* By substituting acetic anhydride for the excess of acetyl chloride used in the nitration, the formation of chlorocreosol can largely be suppressed; the yield of 2-nitrocreosol is, however, if anything diminished.

by rapid crystallisation from a saturated solution (Found : N, 12·1. $C_8H_8O_6N_2$ requires N, 12·3%). It is readily soluble in hot, but only sparingly soluble in cold water, dissolves in aqueous sodium carbonate to a red solution, and gives no coloration with ferric chloride.

Its *acetyl* derivative, obtained by boiling the phenol with excess of acetic anhydride for several hours, crystallises from light petroleum in flat rods, m. p. 53—54°. It is readily soluble in alcohol and gives a pale yellow colour with concentrated sulphuric acid.

The aqueous mother-liquor from the nitration of 2-nitrocreosol was made alkaline with caustic soda, then neutralised with dilute sulphuric acid and extracted with ether. A solid remained after evaporation of the solvent which, when repeatedly crystallised from light petroleum, eventually yielded pure 5 : 6-dinitrocreosol. This observation proves that the 2-nitrocreosol originally used contained a considerable proportion of the 6-nitro-isomeride.

2 : 5-*Dinitrohomoveratrole* (IV).—2 : 5-Dinitrocreosol (0·45 g.) dissolved in dry xylene (7 c.c.) was boiled under reflux with methyl sulphate (0·5 c.c.) and anhydrous potassium carbonate (2 g.). After 30 minutes, a further 0·2 c.c. of methyl sulphate was added, and the liquid was boiled for a further 20 minutes and then worked up in the usual way. When the crude product was distilled, four drops of a nearly colourless oil came over at 190°/15 mm. Its solidification was effected by first cooling in solid carbon dioxide, when it set to a glass, and then transferring it to an ice–salt mixture and scratching vigorously; almost immediate crystallisation then set in.* The solid was obtained in colourless, six-sided plates, m. p. 36°, after two crystallisations from aqueous alcohol (Found : N, 11·5. $C_9H_{10}O_6N_2$ requires N, 11·6%). It gives a pale yellow colour with concentrated sulphuric acid, and the diamine it yields on reduction will not condense with phenanthraquinone to a derivative of phenazine.

2-*Nitrohomoveratrole from* 2-*Nitrocreosol*.—Distillation in steam, followed by repeated fractional distillation in a vacuum, provides a fairly efficient means of separating the two nitrohomoveratroles. The nitrocreosols remaining after all the chlorocreosol had been removed (see p. 1966) were therefore methylated (preferably with methyl iodide) and the methyl ethers were isolated and submitted to steam distillation until the liquid distilling over no longer con-

* This method was applied with equal success to the purified 2-nitrohomoveratrole (see p. 1965) and to 3-nitro-2-methoxyphenyl acetate (Oxford, *loc. cit.*), an oil which had also previously resisted all attempts at crystallisation. This acetate separates from slightly aqueous alcohol in colourless, well-defined, hexagonal tablets, m. p. 29—30°.

tained any trace of oily drops. 6-Nitrohomoveratrole is appreciably volatile in steam (to the extent of 0·5 g. per litre), although much less so than its isomeride. The distillate was kept for several days in the ice-chest, filtered from 6-nitrohomoveratrole, and extracted with ether. A further separation of the two isomerides by repeated fractional distillation in a vacuum is possible, 2-nitrohomoveratrole being slightly the more volatile (Found in the best fraction: C, 54·9; H, 5·6. Calc. for $C_9H_{11}O_4N$: C, 54·8; H, 5·6%). The proportion of 2-nitrohomoveratrole in a given fraction can roughly be estimated by nitration to 2 : 6-dinitrohomoveratrole under the following conditions: The oil (about 1 g.) is nitrated by stirring with nitric acid (*d* 1·42; 3 c.c., previously boiled) for 2·5 minutes (cooling by means of running water). Much water is then added and the precipitate, after standing for a while, is collected in a Gooch crucible, dried, and weighed. Under these conditions, 6-nitrohomoveratrole gives only a 9·7% yield of somewhat impure 5 : 6-dinitrohomoveratrole. Three different specimens of 2-nitrohomoveratrole, prepared from impure 2-nitrocreosol and purified as outlined above, were found to contain at the least 77%, 80%, and 66% of that constituent respectively. On further nitration, they all gave specimens of almost pure 2 : 6-dinitrohomoveratrole with m. p. 85—89° instead of 90—91°.

5 : 6-*Dinitrohomoveratrole*.—According to Oberlin (*loc. cit.*), the direct nitration of 6-nitrohomoveratrole by fuming nitric acid below 5° gives 5 : 6-dinitrohomoveratrole in 36% yield. The present author found the yield could be increased to 60% by allowing a solution of 6-nitrohomoveratrole (0·7 g.) in acetic anhydride (5 c.c.) mixed with nitric acid (*d* 1·42; 1 c.c.) to stand for ½ hour, the temperature being maintained at 0°.

6-*Nitro*iso*creosol* (V).—6-Nitrohomoveratrole (6 g.) was boiled under reflux during 28 hours with a solution of caustic potash (23 g.) in water (150 c.c.). A further quantity of caustic potash solution (6 g. in 25 c.c. of water) was then added, and the boiling continued for a further 9 hours until 6-nitrohomoveratrole could no longer be seen in the condenser. On cooling, the deep red liquid deposited slender, orange needles of the potassium salt of the nitro*iso*creosol. Sufficient water was added to dissolve the crystals, and on addition of dilute sulphuric acid nearly pure 6-nitro*iso*creosol was precipitated. It was crystallised from very dilute hydrochloric acid (charcoal) and then from benzene, from which it separated in long, slender, pale yellow needles, m. p. 168—170°. The nitro-*iso*creosol, m. p. 166—167°, isolated in small amount by Gulland and Robinson (*loc. cit.*) in some experiments on the nitration of *iso*creosol in ethereal solution, must therefore be the 6-nitro-deriv-

ative (Found : C, 52·7; H, 4·9. $C_8H_9O_4N$ requires C, 52·5; H, 4·9%).

6-Nitro*iso*creosol is readily soluble in alcohol and ethyl acetate, moderately easily soluble in chloroform in the cold, and very sparingly soluble in cold benzene and carbon tetrachloride. Its golden-orange solution in saturated aqueous sodium carbonate deposits the bright yellow *sodium* salt on addition of concentrated sodium hydroxide. It gives no coloration with ferric chloride.

Its constitution was proved by methylation to 6-nitrohomoveratrole, the methylation being almost complete after 2 hours' boiling with methyl sulphate, xylene, and potassium carbonate.

The *acetyl* derivative was obtained by boiling the nitrophenol with excess of acetic anhydride for 2 hours. It crystallises from alcohol in pale yellow leaflets, m. p. 98—98·5°, and gives a deep red coloration with concentrated sulphuric acid.

Separation of the Two Nitrohomoveratroles.—When a mixture of about equal quantities of 2- and 6-nitrohomoveratroles is demethylated under the foregoing conditions, the oil remaining unattacked contains less than 5% of 6-nitrohomoveratrole. If the original mixture consists largely of 2-nitrohomoveratrole, the removal of the 6-nitro-isomeride is complete. The accumulated mother-liquors from which crude 6-nitro*iso*creosol had been precipitated by acidification were extracted with ether, and the residue remaining after the evaporation of the solvent was submitted to distillation in steam in the hope of isolating 2-nitro*iso*creosol, but the distillate contained only 6-nitro*iso*creosol, which is slightly volatile in steam.

6-*Bromo-2-nitrohomoveratrole.*—Bromine (6 g.; 1½ equivs.) was added drop by drop with shaking to a solution of 2-nitrohomoveratrole (4·8 g.; 1 equiv., prepared from 2 : 6-dinitrohomoveratrole by Oberlin's method, but not further purified by the alkali treatment) in glacial acetic acid (10 c.c.). Considerable heat was developed. The liquid was kept at room temperature for 48 hours, a considerable proportion of the bromo-derivative crystallising, and then shaken with a large volume of sodium bisulphite solution. The precipitate, after being thoroughly washed with water and dried (yield, 5·8 g. or 86% of the theoretical; m. p. 99—100°), crystallised from methyl alcohol in large, colourless, four-sided tablets, m. p. 102—103° (Found : Br, 28·5. $C_9H_{10}O_4NBr$ requires Br, 29·0%) and was readily soluble in all the usual organic solvents with the exception of cold methyl and ethyl alcohols, and light petroleum, in which it was moderately easily soluble when hot and very sparingly soluble in the cold.

5 : 6-*Dinitro*iso*creosol.*—A solution of the acetyl derivative of 6-nitro*iso*creosol (0·6 g.) in ice-cold nitric acid (*d* 1·5; 3·5 c.c.)

was kept at 0° for 3 hours. Water was then added, and the precipitate collected, washed, and dried (0·2 g.). The filtrate became deep red on the addition of alkali, hence considerable demethylation had taken place. The crude acetyl derivative crystallised from aqueous alcohol in colourless, flat needles, m. p. 109—110°. It was then hydrolysed by warming with sodium carbonate solution and alcohol on the steam-bath. The crude nitrophenol, precipitated by the addition of hydrochloric acid, was recrystallised from water several times, forming very pale yellow, minute, slender needles, m. p. 128—129° (Found : N, 12·3. $C_8H_8O_6N_2$ requires N, 12·3%). It is readily soluble in alcohol, moderately easily soluble in cold benzene, and sparingly soluble in light petroleum and cold carbon tetrachloride. Its orange-coloured solution in saturated aqueous sodium carbonate deposits orange-yellow, flat, pointed rods of the *sodium* salt on addition of concentrated caustic soda. It gives a brownish-red coloration with alcoholic ferric chloride. Its constitution follows from the fact that it yields 5 : 6-dinitrohomoveratrole (m. p. 119—120°) on methylation.

Nitration of 3-*Methoxy*-o-*tolyl Acetate* (VII).—This was carried out according to the details given by Graesser-Thomas, Gulland, and Robinson (J., 1926, 1973) for the preparation of 6-nitro-*m*-methoxy-*p*-tolyl acetate (method B). A solution of nitric acid (1·8 c.c.; *d* 1·4) in acetic anhydride (2 c.c.) to which a few small crystals of urea had been added was very slowly introduced, drop by drop, into a mixture of the acetate (2·5 g.) and acetic anhydride (2·5 c.c.) cooled to — 15°. Addition of water after 15 minutes precipitated an oil, which was hydrolysed by warming it on the steam-bath with *N*-caustic soda. Acidification with dilute sulphuric acid then precipitated an oil; this, after a tedious treatment with light petroleum followed by two crystallisations from water, yielded a minute quantity of a substance, m. p. 60—61°, which crystallised from water in colourless, silky needles, gave no coloration with ferric chloride, and dissolved in saturated sodium carbonate to a golden-yellow solution. It was probably 4-nitro-*o*-creosol, since it yielded a nitrophenol when nitrated in acetic acid solution, the aminophenol from which condensed with phenanthraquinone to give a derivative of phenazine which gave a dull cherry-red colour with concentrated sulphuric acid and exhibited a perceptible green fluorescence in benzene solution (compare the behaviour of 3 : 4-dinitroguaiacol; Oxford, *loc. cit.*).

The various aqueous mother-liquors from the foregoing operations were extracted with ether, the extract was added to the light petroleum mother-liquors, and the residue remaining after evaporation of the combined extracts was methylated by the xylene–

methyl sulphate–potassium carbonate method. The methyl ethers were nitrated by heating them on the steam-bath for 10 minutes with a considerable excess of fuming nitric acid diluted with an equal volume of glacial acetic acid. Addition of water then precipitated almost pure 4 : 5-dinitro-*o*-homoveratrole, m. p. 125—127° after one crystallisation from alcohol (Majima and Okazaki, *loc. cit.*, record m. p. 126—127°). Further proof of the position of the nitro-groups was afforded by condensing the diamine obtained by reduction with zinc and hydrochloric acid, with phenanthraquinone; a substance exhibiting all the colour reactions of a 1 : 2-dimethoxyphenanthraphenazine was then obtained.

I wish to thank Professor R. Robinson, F.R.S., for his continued interest in this work and for many helpful suggestions during its progress.

THE UNIVERSITY, MANCHESTER. [*Received, June 11th*, 1927.]

CCLVII.—*Nitration of β-Naphthyltrimethylammonium Nitrate.*

By BERTRAM HOBART INGHAM.

IT has been shown by Vorländer and Sieberts (*Ber.*, 1919, **52**, 283) that in simple benzene derivatives the positively charged ammonium group in immediate proximity to the nucleus has an almost exclusive meta-orienting effect. This is a particular example of the generalisation, first enunciated by Robinson, that a positively charged group in immediate proximity to the nucleus always conduces to the formation of a high proportion of meta-substitution products. The former authors showed that on nitration of phenyltrimethylammonium nitrate or bromination of the bromide the corresponding meta-derivatives were produced, whilst *o*-, *m*-, and *p*-tolyltrimethylammonium nitrates yield, on nitration, 5-nitro-2-tolyl-, 4-nitro-3-tolyl-, and 3-nitro-4-tolyl-ammonium nitrates respectively. The so-called "effect" of this group is therefore strongly opposed to that of hydroxyl or methoxyl. In β-naphthol and its methyl ether the positions most readily substituted are precisely those which may be deduced from the simplest application of the rule of alternation, namely 1, 8, 6, and 3, and on such grounds it must be inferred that substitution at these positions in β-naphthyltrimethylammonium salts will occur less readily than in the corresponding positions in naphthalene itself. The simple rules of alternation, however, give no clue as to which of the remaining positions, namely, 7, 5, or 4, will be most readily attacked. It is well known that, in the

naphthalene series, substitution occurs preferentially in the α-positions, and therefore positions 5 and 4 are more probable points of substitution than position 7. There remains yet a choice to be made between positions 5 and 4. If the action of the "meta-directive" group is to assist in the process of substitution in any way, then, other things being equal, the nucleus containing the directive group should be the more susceptible to substitution (as is the case with the two naphthols, for example). On the contrary, if its influence be inhibitory, and if the inhibition applies not only to the ortho- but also to the meta-position (to a smaller extent), then such influence should be most effective in the nucleus to which the group is attached, and position 5, being less affected than position 4, should be the more susceptible to substitution.

The author's experiments emphatically support the latter view, which, moreover, is entirely consistent with the results obtained in the schools of H. E. Armstrong and of A. F. Holleman. The product obtained on nitration of β-naphthyltrimethylammonium nitrate was nearly pure 5-nitro-β-naphthyltrimethylammonium nitrate in almost theoretical yield.

EXPERIMENTAL.

β-Naphthyltrimethylammonium iodide was prepared by a method similar to those of Bamberger (*Ber.*, 1889, **22**, 1306) and of Morgan (J., 1900, **77**, 882), but it was found to be unnecessary to heat the reactants in a sealed tube, refluxing for 3½ hours (in a copper flask) and allowing the crude product to stand over-night before purification being found to give practically as good a yield (approx. 60%). The substance was purified by extraction with and crystallisation from water, followed by recrystallisation from alcohol; it was thus obtained in colourless, hexagonal plates, m. p. 193° (decomp.).

The *nitrate* and the *picrate* were obtained by double decomposition from the iodide with silver nitrate and with picric acid, respectively; they crystallised from water, the nitrate in colourless, rectangular plates, m. p. 190° (decomp.), and the picrate in golden-yellow needles, m. p. 194—195° (decomp.).

Nitration of β-Naphthyltrimethylammonium Nitrate.—The salt was dissolved in three times its weight of 99% nitric acid (*d* 1·52) with water-cooling, a vigorous momentary reaction taking place. After having stood at room temperature for 2 hours, the solution was poured on 1½—2 times its weight of ice, and the product made almost neutral * with (solid) sodium bicarbonate, separation of the

* The substance acts as its own indicator, any alkalinity (even that of sodium bicarbonate) producing an intense red colour.

nitro-compounds proceeding with the neutralisation. The yield was almost theoretical. After two crystallisations from water and one from aqueous alcohol, a *mononitro-β-naphthyltrimethylammonium nitrate* was obtained in orange-yellow, rectangular prisms, m. p. 231° (decomp.) (Found: C, 52·5; H, 5·6; N, 14·4. $C_{13}H_{15}O_5N_3$ requires C, 53·2; H, 5·1; N, 14·3%). The nitrate was homogeneous, for when it was subjected to fractional crystallisation and subsequent conversion into the iodide, followed by refractionation, no difference in melting point or in appearance under a polarising microscope of any of the fractions could be detected.

The *iodide* was obtained from water in golden-yellow, rectangular prisms, m. p. 194° (decomp.) (Found: I, 35·9. $C_{13}H_{15}O_2N_2I$ requires I, 35·5%). The *picrate* was obtained from aqueous acetone in canary-yellow, rectangular prisms, softening from 248°, m. p. 254° (decomp.).

Unsuccessful attempts were made to determine the constitution of this nitration product of β-naphthyltrimethylammonium nitrate by oxidation, and also by treatment with concentrated aqueous solutions of alkalis, which caused the substance to undergo a peculiar and complicated change. In the circumstances, it was decided to proceed by synthesis as described below.

Methylation of 5-Nitro-β-naphthylamine.—5-Nitro-β-naphthylamine (Friedländer and St. Szymanski, *Ber.*, 1892, **25**, 2076) (1 mol.) in benzene (15 parts by weight) and methyl sulphate (4 mols.) in benzene (4 parts) were mixed and refluxed for 6½ hours, a dirty-white solid gradually separating. Next day, the precipitate was collected, washed with benzene, and boiled with water (100 parts), and the aqueous extract was cooled and made alkaline with ammonia, whereby the methylated bases were precipitated. The filtered solution, which contained 5-nitro-β-naphthyltrimethylammonium methosulphate, was divided into two portions, one of which was converted into the *iodide* (Found by micro-analysis: N, 8·4. $C_{13}H_{15}O_2N_2I$ requires N, 7·8%) and the other into the *picrate* by means of sodium iodide and picric acid, respectively.

Comparative and mixed m. p. tests showed that the nitration product of β-naphthyltrimethylammonium nitrate was 5-nitro-β-naphthyltrimethylammonium nitrate (see table).

As the yield of the quaternary salt obtained in the methylation experiment was very small, and also for comparative purposes, it was considered desirable to methylate the 8-nitro-isomeride and thereby furnish conclusive proof that the above quaternary salt was derived from 5-nitro-β-naphthylamine, and not from any impurity in it. The methylation was performed in the same way as that of the 5-isomeride.

Melting points of Nitro-β-naphthyltrimethylammonium Salts.

	5-Iso-meride.	8-Iso-meride.	Corresponding salt (X) from nitration product.	5-Iso-meride mixed with X.	8-Iso-meride mixed with X.
Iodide (1st sample)	189°	180°	192°	190°	180°
(2nd sample)	190	—	191	191	—
Picrate (1st sample)	254*	221—223	254*	254*	212—218
(2nd sample)	254*	221—223	254*	254*	212—229

* With softening from approximately 248° in each case.

The discrepancies of one or two degrees between some of the melting points given in the table and those of the corresponding substances given hitherto are due to the rate of heating; the m. p.'s in the table are strictly comparable, for they were taken simultaneously in the same bath.

The author wishes to express his thanks to Professor Lapworth for his interest in the investigation.

THE UNIVERSITY, MANCHESTER. [*Received, July 6th*, 1927.]

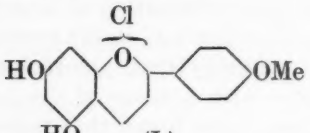
CCLVIII.—*A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part XII.*

By DAVID DOIG PRATT, ALEXANDER ROBERTSON, and ROBERT ROBINSON.

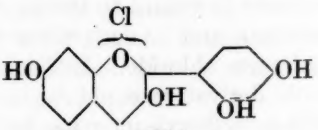
WHEN acacetinidin chloride (I) (Part IV, Pratt, Robinson, and Williams, J., 1924, **125**, 200) was demethylated, it yielded a very well-characterised trihydroxyflavylium chloride which had the reactions but not the crystalline form of apigeninidin chloride prepared by demethylation of its trimethyl ether (Part VI, J., 1925, **127**, 1133). The properties of the two specimens were closely similar, but not identical in every respect, and for this reason there was a doubt in regard to the course of the condensation of benzoylacetaldehyde and its derivatives with phloroglucinol in the presence of hydrogen chloride. Hitherto no unmethylated phloroglucinaldehyde derivative could be condensed with ketones of the form $CH_3{\cdot}CO{\cdot}R$ to flavylium salts, but we have now found that *O*-benzoylphloroglucinaldehyde (this vol., p. 1713) can be utilised for this purpose. With *p*-methoxyacetophenone, it gives a benzoylacacetinidin chloride, and, after hydrolysis with methyl-alcoholic ammonia and subsequent treatment with hydrochloric acid, acacetinidin chloride, identical with the salt already described, was obtained. There is, therefore, no doubt that the condensation of anisoylacet-

aldehyde and phloroglucinol proceeds normally and does not, as was at one time suspected, give rise to an *epi*flavylium derivative. The specimen of apigeninidin chloride, prepared as described in this communication, is unquestionably more pure than that which was obtained previously by demethylation of the trimethyl ether. These results have been confirmed in the chrysinidin series and one and the same chrysinidin has been obtained on the one hand by the condensation of benzoylacetaldehyde and phloroglucinol, and on the other by hydrolysis of the benzoylchrysinidin chloride derived from *O*-benzoylphloroglucinaldehyde and acetophenone.

The condensation of benzoylacetaldehyde with acetophenone by means of hydrogen chloride in acetic acid solution was first described by Bülow and Sicherer (*Ber.*, 1901, **34**, 3896). The quantity of acetic acid employed was not stated, but the red product, $C_{15}H_{13}O_4Cl$, was very sparingly soluble in organic solvents and soon separated from the reaction mixture. These authors do not mention the necessity for any special precautions in carrying out the process, and in the first attempts which we made to repeat it the product was invariably an ochre-red, very sparingly soluble substance which separated quickly in almost quantitative amount. This substance can be easily prepared by adding phloroglucinol and benzoylacetaldehyde in molecular proportion to formic acid or by adding a few drops of hydrochloric acid to an acetic acid solution of the components. It appears to have the composition $C_{30}H_{22}O_7$ and, on treatment with a boiling mixture of acetic and hydrochloric acids, it slowly passes into chrysinidin chloride. Later it was found that the Bülow condensation could be effected in ethereal solution, and also in acetic acid solution if the materials were free from water and access of moisture to the reaction mixture was prevented. In the latter case, the dark reddish-brown product had the composition $C_{15}H_{11}O_3Cl$ and only began to separate after some hours. An account of the preparation of resomorinidin chloride (II) is included in this communication.



(I.)



(II.)

EXPERIMENTAL.

Trianhydrobisbenzoylacetaldehydephloroglucinol. — Cold filtered solutions of benzoylacetaldehyde (2·9 g.) in formic acid (5 c.c.) and of phloroglucinol (2·5 g.) in formic acid (40 c.c.) were mixed; an orange-red product soon began to separate. After 2 hours,

water was added and the substance was collected, washed, and dried at 100° (Found: C, 72·9, 73·2; H, 4·5, 4·6. $C_{30}H_{22}O_7$ requires C, 72·8; H, 4·5%). The yield was 5·1 g., and only when relatively more phloroglucinol was employed could the phenol be detected in the filtrate. The substance can also be obtained by addition of a few drops of hydrochloric acid to a solution of the components in equimolecular proportion in acetic acid or by passing hydrogen chloride into an acetic acid solution of benzoylacetaldehyde and phloroglucinol without precautions aimed at the exclusion of water. Attempts to crystallise this very sparingly soluble compound were unsuccessful. On heating, the substance darkens slightly from 210—280° and above this temperature gradually chars without melting.

Chrysinidin Chloride (5 : 7-*Dihydroxyflavylium Chloride*).—(A) The product of condensation of benzoylacetaldehyde and an equivalent amount of anhydrous phloroglucinol in ethereal solution by means of hydrogen chloride in the cold during 4 hours was collected and extracted with boiling dilute hydrochloric acid. The salt crystallised from the hot filtrates (poor yields) in reddish-brown prismatic needles, which were dried over sulphuric acid (Found: C, 58·7; H, 4·7. $C_{15}H_{11}O_3Cl,2H_2O$ requires C, 58·1; H, 4·8%). This salt darkens at 250° but does not melt at 300°. Its yellow solution in concentrated sulphuric acid does not fluoresce, nor do the orange-red alcoholic solutions exhibit this property. The salt is sparingly soluble in aqueous hydrochloric acid (even 0·05%) and dissolves in aqueous sodium carbonate to a deep brownish-red solution which is orange in thin layers. Sodium hydroxide gives the same colour, but the solutions soon become orange, especially on heating.

(B) A solution of the salt was obtained by boiling the orange-red compound, $C_{30}H_{22}O_7$, for 6 hours with an excess of a mixture of acetic acid (2 vols.) and concentrated hydrochloric acid (1 vol.). Water was added, and the perchlorate precipitated from the filtered solution.

(C) A solution of anhydrous phloroglucinol (5 g.) and benzoylacetaldehyde (8 g.) in pure glacial acetic acid (35 c.c.) was saturated with hydrogen chloride in an apparatus designed to exclude moist air, and then kept for 12 hours. The deep reddish-brown crystals which slowly separated were collected, washed with acetic acid, and dried over sodium hydroxide in a vacuum (Found: C, 65·6, 65·4; H, 4·4, 4·1. $C_{15}H_{11}O_3Cl$ requires C, 65·6; H, 4·0%). The yield was 2 g. By adding ether to the filtrate a solid was precipitated which was extracted by boiling 0·5% hydrochloric acid; this gave a further 2·2 g. of chrysinidin chloride and left 5·5 g. of a dark red, insoluble material.

(D) A cold solution of *O*-benzoylphloroglucinaldehyde (1·6 g.) and acetophenone (3 g.) in dry ethyl acetate (30 c.c.) was saturated with hydrogen chloride and kept for 3 days. The orange-red liquid acquired a greenish-yellow fluorescence and gradually deposited crystals (2 g.). The orange *O*-benzoylchrysinidin chloride (1·9 g.) was dissolved in methyl alcohol (100 c.c.) and the solution was saturated with ammonia at 0° and kept at this temperature for 24 hours. The ammonia and methyl alcohol having been removed under diminished pressure at room temperature, the residue was dissolved in warm methyl alcohol (20 c.c.), and hot hydrochloric acid (40 c.c.) added. The amorphous precipitate was collected and extracted with boiling 0·5% hydrochloric acid, and the salt again precipitated from the filtered solution by the addition of concentrated hydrochloric acid. It was now partly crystalline and was converted into the perchlorate, which was fully purified.

Chrysinidin perchlorate. The various specimens of chrysinidin chloride have been identified with each other by conversion into this characteristic derivative, which crystallises from acetic acid in glistening, deep red, rectangular, prismatic needles (Found in material from B above: C, 53·3; H, 3·4. $C_{15}H_{11}O_7Cl$ requires C, 53·2; H, 3·3%). The substance darkens at 208° and melts with decomposition at 244°. It is very readily soluble in alcohol and on the addition of aqueous perchloric acid the substance crystallises in slender, glistening, orange-red needles. Careful comparison showed that all the specimens were identical; on the other hand, the chrysinidin obtained by demethylation of the dimethyl ether (Part VI, *loc. cit.*) must have been contaminated with methoxy-containing salts, since the perchlorate decomposed at 185°.

O-*Benzoylacacetinidin Chloride.*—A solution of *O*-benzoylphloroglucinaldehyde (0·6 g.) and *p*-methoxyacetophenone (2 g.) in dry ethyl acetate (30 c.c.) was saturated in the cold with hydrogen chloride; in the course of an hour it became deep orange and exhibited a striking greenish-yellow fluorescence. The mixture was kept for 3 days and the salt which had separated was then collected (2 g.); a further quantity (0·5 g.) was obtained by addition of ether to the filtrate. Concentrated hydrochloric acid was added to a solution of the salt in a hot mixture of equal volumes of alcohol and 0·5% hydrochloric acid until a faint turbidity appeared; on cooling, the substance crystallised in bright, orange-red sheaves of slender, prismatic needles (Found in material dried over sulphuric acid: C, 64·6; H, 4·7. $C_{23}H_{17}O_5Cl,H_2O$ requires C, 64·7; H, 4·5%). The alcoholic solutions of this benzoylacetinidin chloride are orange to orange-red and exhibit strong green fluorescence.

Acacetinidin Chloride (I).—The debenzoylation of benzoylacacetin-

idin chloride (3 g.) was accomplished in much the same way as described above in the case of benzoylchrysinidin chloride and the crude acacetinidin chloride (1·5 g.) was crystallised by solution in hot 0·5% hydrochloric acid and addition of concentrated hydrochloric acid until turbidity appeared. After three such processes, the salt was obtained in microscopic, reddish-brown balls. It was then crystallised by addition of concentrated hydrochloric acid to an alcoholic solution and obtained in prismatic needles, and on repetition in diamond-shaped and rhombic plates with a brilliant green reflex but exhibiting much twinning. A third crystallisation in this way gave clear-cut, individual crystals having a form identical with that of crystals of acacetinidin chloride (Part IV, *loc. cit.*). The reactions of the two specimens were also identical and in addition the perchlorates and picrates were examined and compared, with the result that no difference could be detected between the specimens of the respective derivatives obtained from benzoylacacetinidin chloride from acacetinidin chloride.

Acacetinidin perchlorate crystallised from hot aqueous perchloric acid in red, glistening, slender, prismatic needles and from acetic acid in red, elongated, pointed prisms having a bluish-green reflex. The substance darkens at 260° and melts at 278—280° (decomp.). A mixture of the two specimens behaved in the same way.

Acacetinidin picrate crystallised from 40% alcohol, containing picric acid, in long, red, prismatic needles which darkened at 220—225° and melted to a black liquid at 231—233° (mixed—the same).

Apigeninidin Chloride (5 : 7 : 4′-*Trihydroxyflavylium Chloride*).—Acacetinidin chloride (2·1 g.) was demethylated by gently boiling with hydriodic acid (60 c.c.; *d* 1·7) and phenol (9 g.) in a stream of carbon dioxide. Methyl iodide was rapidly evolved and after 15 minutes the acacetinidin iodide had passed into solution. The reaction was continued for a further 10 minutes; a test then proved that only traces of methyl iodide were being produced. On cooling, the apigeninidin iodide quickly crystallised in scarlet, prismatic needles and these were collected on asbestos, washed with ether, and dried at 100° (2·2 g.). The substance is readily soluble in hot alcohol and on the addition of hydrochloric acid the chloride crystallises from the solution, but in order to ensure complete conversion the following method was adopted. The iodide (2·2 g.) and silver chloride (about 10 g.) were added to ethyl alcohol (400 c.c.) and concentrated hydrochloric acid (5 c.c.), and the solution was boiled during 10 minutes, filtered and mixed with concentrated hydrochloric acid (50 c.c.). On cooling, apigeninidin chloride separated in very well-shaped, glistening, rhombic prisms. Individual crystals are seen under the microscope to be light orange-yellow by transmitted

light and the mass is bright salmon-red. The substance was washed with alcohol and dried in a vacuum (Found: C, 58·5; H, 4·4. $C_{15}H_{11}O_4Cl,H_2O$ requires C, 58·4; H, 4·2%). This hydrate is very stable and when quickly heated appears to suffer no change below 200°. At about 230° it darkens and turns green. The anhydrous substance chars above 350° but does not melt. Prolonged heating at 100° does not effect dehydration, but at 140° in a vacuum the substance loses weight and becomes hæmatite-red.

Apigeninidin chloride is sparingly soluble in hot dilute hydrochloric acid and in most organic solvents. On boiling with not too much water, it dissolves and at once separates again as a flocculent precipitate consisting of orange, microscopic needles. This substance is a basic chloride and on the addition of a drop of hydrochloric acid is converted into the normal salt, recognised by its characteristic mode of crystallisation in rhombic prisms. *n*-Butyl or *iso*amyl alcohol extracts most of the salt from aqueous solution, giving an orange-red solution, but the aqueous layer always retains a canary-yellow colour. This behaviour differs from that of pelargonidin chloride, which is completely extracted from aqueous solution by *iso*amyl alcohol. The bright yellow solution in concentrated sulphuric acid exhibits an intense green fluorescence. The colour base, obtained by the action of sodium acetate on the chloride in aqueous solution, is a brownish-red precipitate, sparingly soluble in butyl alcohol to an eosin-red solution. On great dilution, the yellow solutions of apigeninidin salts become red, but under no conditions is a colourless pseudo-base formed. The chloride or the colour base dissolves in aqueous sodium carbonate or ammonia to a rich crimson solution, the colour of which is much bluer, brighter and more persistent on dilution than that of an alkaline solution of acacetinidin chloride. The orange-red solution in alcohol becomes intense yellowish-brown on the addition of ferric chloride. The ferrichloride could not be obtained because it is more soluble than the chloride. For example, a suspension of the chloride in boiling acetic acid gives a clear solution on the addition of a little ferric chloride dissolved in concentrated hydrochloric acid, but on cooling the chloride separates. The *mercurichloride* is extremely sparingly soluble in dilute hydrochloric acid containing mercuric chloride and crystallises in hair-like, orange, microscopic needles. The chloride dissolves somewhat readily in hot dilute perchloric acid and on quickly cooling the *perchlorate* separates in very slender, long, irregular fibres which, on standing in contact with the solvent, change into very dense clusters of microscopic needles. The *periodide* behaves similarly, being precipitated as a stringy, dark brown mass which is resolved into slender needles. Numerous attempts to

oxidise apigeninidin to apigenin were fruitless. The alkaline solution retains its colour when air is aspirated through it during 12 hours.

Hydroxymethyleneacetoveratrone.—Methyl alcohol (1·6 g.) was added to a suspension of granular sodium (1·1 g.) in dry ether (50 c.c.) and when the formation of alkyloxide was complete a mixture of ethyl formate (5·2 g.) and acetoveratrone (9·7 g.) was slowly introduced with frequent shaking; a white, pasty mass was formed. Next day, ice, acetic acid, and ether were added and the separated ethereal solution was shaken with a concentrated solution of copper acetate. The *copper* derivative (7·0 g.) crystallised from toluene in pale green needles which softened at 180° and decomposed at 188° (Found: Cu, 13·0. $C_{22}H_{22}O_8Cu$ requires Cu, 13·3%). Similarly, the *copper* derivative of hydroxymethylene-2:4-dimethoxyacetophenone was obtained from resacetophenone dimethyl ether (yield, 13 g. from 14 g. of the ketone). It crystallised from toluene in pale green prisms, m. p. 190° (Found: Cu, 13·4%).

5:7-*Dihydroxy*-3′:4′-*dimethoxyflavylium Chloride.*—An ethereal solution of hydroxymethyleneacetoveratrone (itself an oil exhibiting the usual properties of its class) was obtained by shaking the copper derivative (5·5 g.) with dilute sulphuric acid and ether; the separated ethereal layer was dried with sodium sulphate. This solution was added to one of anhydrous phloroglucinol (3 g.) in ether, and a stream of hydrogen chloride led through the mixture for 4 hours. After 12 hours, the bright red condensation product was collected, washed with ether, and dried (5 g.). This product was boiled under reflux with alcohol (1500 c.c.) and concentrated hydrochloric acid (12 c.c.) for an hour, and the solution distilled until separation of the salt commenced. After keeping for 24 hours, the solid was collected and further purification was effected by solution in and separation from 2% hydrochloric acid. After several such processes, the substance crystallised in a homogeneous form in opaque, microscopic, spherical masses. Further slow crystallisation from hot dilute solutions gave reddish-brown, prismatic needles which decomposed at 272° (Found in material dried in a vacuum over sulphuric acid: C, 56·4; H, 4·8. $C_{17}H_{15}O_5Cl,1·5H_2O$ requires C, 56·5; H, 4·9%). This salt dissolves in aqueous sodium carbonate to an intense blood-red solution.

Demethylation. A mixture of this luteolinidin dimethyl ether (1·4 g.) with phenol (4 g.) and concentrated hydriodic acid (30 c.c.) was boiled in an atmosphere of carbon dioxide for 30 minutes. A bright red iodide crystallised from the solution and this was collected and converted in the usual manner into the corresponding *chloride.* The latter crystallised from alcohol in small, orange-red needles,

which decomposed at 282° (Found in material dried in a vacuum over sulphuric acid: C, 58·6; H, 3·4; MeO, 10·5; Cl, 10·1; loss at 105° in a high vacuum, 2·7. $C_{16}H_{12}O_5Cl,0{\cdot}5H_2O$ requires C, 58·4; H, 3·7; 1MeO, 9·5; Cl, 10·7; H_2O, 2·8%). The substance is therefore a luteolinidin chloride monomethyl ether. It gives a Bordeaux-red to reddish-purple solution in aqueous sodium carbonate and its acid solutions have the same colour as those of luteolinidin chloride. The alkali colour reaction provides the only available evidence in regard to constitution and suggests that the salt is 5 : 7 : 4′-trihydroxy-3′-methoxyflavylium chloride rather than the possible isomeride. The purified substance must contain a trace of luteolinidin chloride, since it gives a weak ferric chloride reaction. On further demethylation with a mixture of hydriodic acid (*d* 1·75) and phenyl acetate, during the course of which the rate of evolution of methyl iodide was observed, luteolinidin iodide was obtained. The corresponding chloride showed all the reactions and properties of the substance previously obtained from luteolinidin chloride trimethyl ether (Part VI, *loc. cit.*).

7-*Hydroxy*-3 : 2′ : 4′-*trimethoxyflavylium Chloride*.—A solution of ω : 2 : 4-trimethoxyacetophenone (4·4 g.) and β-resorcylaldehyde (2·8 g.) in dry ether (100 c.c.) was saturated with hydrogen chloride for 2 hours and kept over-night. The product separated in orange-red needles with a dark green reflex (8 g.). It crystallised from dilute hydrochloric acid in crimson, prismatic needles which darkened at 140° and decomposed at 185° (Found in material dried in a vacuum over sulphuric acid: C, 58·8; H, 5·4. $C_{18}H_{17}O_5Cl$ requires C, 59·0; H, 5·2%). The colour base is bluish-red, a pseudo-base is readily formed, and the yellow solution in concentrated sulphuric acid exhibits bright apple-green fluorescence.

3 : 7 : 2′ : 4′-*Tetrahydroxyflavylium Chloride* (*Resomorinidin Chloride*) (II).—A mixture of the trimethyl ether (4 g.), phenol (8 g.), and hydriodic acid (80 c.c.; *d* 1·7) was gently boiled during 35 minutes in a stream of carbon dioxide. On cooling, glistening prismatic needles, exhibiting golden-green reflex, separated and these were collected and dried (2·8 g.). Conversion into chloride by means of silver chloride and a trace of hydrogen chloride was accomplished in alcoholic solution and, on the addition of 10% aqueous hydrochloric acid to the filtrate, the salt crystallised in small, red needles which decomposed at 216° (Found in material dried in a vacuum over sulphuric acid: C, 54·3; H, 4·2. $C_{15}H_{11}O_5Cl,1{\cdot}5H_2O$ requires C, 54·0; H, 4·2%). Resomorinidin chloride is very sparingly soluble in cold dilute hydrochloric acid and moderately easily soluble in the hot solvent to an orange-red solution. Its solution in sulphuric acid exhibits bright apple-green

fluorescence. Sodium carbonate added to an aqueous solution gives an intense reddish-violet or permanganate-like coloration. An alcoholic solution of the salt is bluish-red and on addition of sodium carbonate becomes dichroic, red in thick layers, blue in thin layers, and exhibits dark red fluorescence. A hydrochloric acid solution was decolorised on boiling with zinc dust, and the cooled mixture was then extracted with ether. Addition of very dilute sodium hydroxide to the separated ethereal layer gave a blue solution which soon became violet and then rose-coloured. On warming, the aqueous layer became greenish-yellow and developed an intense ivy-green fluorescence.

Ethyl 2 : 4 : 6-*Trimethoxybenzoylpyruvate*, $C_6H_2(OMe)_3 \cdot CO \cdot CH_2 \cdot CO \cdot CO_2Et$. —This substance was prepared in the hope that it might prove to be a convenient source of 5 : 7-dimethoxychromone, which was required in connexion with attempts to obtain representatives of the *epi*flavylium series. Phloracetophenone trimethyl ether (5·2 g.) (Kostanecki and Tambor, *Ber.*, 1899, **32**, 2261) and ethyl oxalate (5·5 g.) were added to an absolute alcoholic solution (30 c.c.) of sodium ethoxide (1·4 g. of sodium) and next day ether was added to complete the separation of the sodium derivative. This was collected and dissolved in water and the *ester*, liberated by means of acetic acid, was isolated (5 g.); it crystallised from aqueous alcohol in long, pale yellow needles, m. p. 84° (Found: C, 58·3; H, 5·9. $C_{15}H_{18}O_7$ requires C, 58·1; H, 5·8%). This ester exhibits the usual properties of its class and in the solid state, preferably as a well dispersed precipitate suspended in a faintly acid medium, forms a highly characteristic blue compound with iodine.

The authors wish to thank the Royal Society and the Chemical Society for grants which have defrayed a part of the cost of the investigation.

THE UNIVERSITY OF MANCHESTER. [*Received, June 21st*, 1927.]

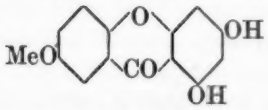
CCLIX.—*The Constitution of Gentisin.*

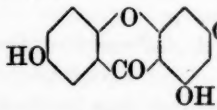
By JUNZO SHINODA.

GENTISIN was first isolated from gentian root by Henry and Caventou (*J. Pharm. Chim.*, 1821, 178) and was subsequently examined by Baumert (*Annalen*, 1847, **62**, 106) and by Hlasiwetz and Habermann (*ibid.*, 1875, **175**, 63; 1876, **180**, 343). The investigations of Kostanecki and his co-workers have proved that gentisin is the monomethyl ether of gentisein, which is 1 : 3 : 7-

trihydroxyxanthone and was synthesised by Kostanecki and Tambor (*Monatsh.*, 1894, **15**, 1) by condensation of phloroglucinol and quinolcarboxylic acid. An attempt of these investigators to obtain 1 : 3-dihydroxy-7-methoxyxanthone along similar lines was unsuccessful (*Monatsh.*, 1895, **16**, 920). Kostanecki, however, showed that gentisein on methylation yields gentisin and that gentisin yields only a monomethyl ether. This excludes the possibility that gentisin is 3 : 7-dihydroxy-1-methoxyxanthone and this substance must therefore be 1 : 3-dihydroxy-7-methoxyxanthone (I) or 1 : 7-dihydroxy-3-methoxyxanthone (II).

(I.)





(II.)

From the behaviour of bisazobenzene-gentisin, Perkin (J., 1898, **73**, 1028) has indicated that gentisin should be represented by the formula (II), and the present author now confirms this conclusion, since the compound (I) described in this communication is quite different from gentisin. The methyl group of gentisin is thus in a position similar to that which it occupies in rhamnetin and rhamnazin. The synthesis of (I) has been effected by an application of the Hoesch reaction following the similar preparation of 1 : 3-dihydroxyxanthone by Nishikawa and Robinson (J., 1922, **121**, 839).

Experimental.

2-Hydroxy-5-methoxybenzaldoxime, obtained in the usual manner from 2-hydroxy-5-methoxybenzaldehyde, crystallised from water in colourless, prismatic needles, m. p. 118° (Found: C, 57·4; H, 5·8. $C_8H_9O_3N$ requires C, 57·4; H, 5·4%). *2-Hydroxy-5-methoxybenzonitrile*, obtained on treatment of the oxime with boiling acetic anhydride for 3 hours and subsequent hydrolysis with 10% sodium hydroxide solution, crystallised from water in colourless needles, m. p. 136° (Found: C, 64·0, 64·5; H, 5·0, 4·7. $C_8H_7O_2N$ requires C, 64·4; H, 4·7%).

1 : 3-*Dihydroxy-7-methoxyxanthonimine Hydrochloride*.—A mixture of 2-hydroxy-5-methoxybenzonitrile (5 g.), anhydrous phloroglucinol (4 g.), zinc chloride (5 g.), and dry ether (30 c.c.) was saturated with hydrogen chloride with frequent shaking. After a few hours, yellow crystals separated, but later these gave place to a deep yellow solution and then to orange crystals. After 10 days, water was added and the insoluble material (A) collected. The filtrate was extracted with ether and then concentrated; on cooling, yellow crystals (B) separated (Found: HCl, 12·1. $C_{14}H_{12}O_4NCl$ requires HCl, 12·4%). The properties of (A) and (B) are very similar; both

are very sparingly soluble in most organic solvents and dissolve in concentrated sulphuric acid to a yellow solution which exhibits green fluorescence. The solution in aqueous alkalis is yellow.

1 : 3-*Dihydroxy*-7-*methoxyxanthone* (I).—The ketimine hydrochloride was hydrolysed by means of boiling aqueous sodium hydroxide (until ammonia was no longer evolved) and the *iso*-*gentisin* was then precipitated by the addition of dilute sulphuric acid as a gelatinous mass that became crystalline when the liquid was boiled. The substance crystallised from aqueous alcohol in elongated, yellow plates, m. p. 241° (Found: C, 64·8; H, 4·3. $C_{14}H_{10}O_5$ requires C, 65·1; H, 3·9%).

The yellow solution in concentrated sulphuric acid exhibits green fluorescence, and ferric chloride added to an alcoholic solution develops a greenish-black coloration. The substance does not reduce an ammoniacal silver nitrate solution. A distinction from gentisin is that when an alkaline solution is agitated with sodium amalgam it becomes, like gentisein, blood-red; gentisin gives a deep green coloration under these conditions. On acetylation, a *derivative*, m. p. 211—212°, was obtained.

The *iso*gentisin was demethylated by means of boiling hydriodic acid; the gentisein obtained crystallised from methyl alcohol in orange-yellow needles, m. p. 318° with darkening from 310°. The substance had the properties attributed to it by Kostanecki and on acetylation gave the triacetyl derivative; this crystallised from acetic acid in white, silky needles which, alone or mixed with a specimen obtained by Kostanecki's method (*Monatsh.*, 1891, **12**, 205), melted at 226°.

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CCLX.—*Syntheses of Cyclic Compounds. Part I. Ethyl βγ-Dimethylbutane-aaδδ-tetracarboxylate and some* cyclo*Butane Compounds derived therefrom.*

By ISRAEL VOGEL.

IN extending his investigations on the reduction of unsaturated compounds by moist aluminium amalgam (this vol., p. 594), the author has been led to examine the reduction of esters of the type $CR'R'':CX\cdot CO_2Et$ (I), where X may be CO_2Et, COMe, or CN, and R',R'' may be Me,H; Ph,H; Me,Me; or the *cyclo*pentane or *cyclo*hexane ring. Coupling would presumably take place in the β-positions (compare Vogel, *loc. cit.*), resulting in the formation of compounds

II) which (if $X = CO_2Et$) are homologues, symmetrically substituted in the β- and γ-positions, of ethyl butanetetracarboxylate, a

(II.) $\begin{matrix} CR'R''\cdot CHX\cdot CO_2Et \\ CR'R''\cdot CHX\cdot CO_2Et \end{matrix}$ $\qquad$ $\begin{matrix} CHMe\cdot CH(CO_2Et)_2 \\ CHMe\cdot CH(CO_2Et)_2 \end{matrix}$ (III.)

substance which has found wide application as a synthetic agent in the hands of Professor Perkin and his collaborators (see numerous papers in J., 1884—1900). This series of researches has therefore been instituted with the following objects: (1) to synthesise compounds of the type (II); (2) to study the influence of groups and rings in the β- and γ-positions on (*a*) the relative ease of formation and stability of four-, five-, six-, and higher-membered rings by condensation with the appropriate reagents, and (*b*) the stability of the *cis*- and *trans*-anhydrides of the cyclic dibasic acids; (3) to synthesise substituted adipic acids from compounds of the type (II) and to employ them in the investigation of the stability of the *cis*- and *trans*-anhydrides as well as of their simpler cyclic derivatives.

The present communication is concerned with the reduction of ethyl ethylidenemalonate by moist aluminium amalgam.* This substance has been previously reduced by means of moist sodium amalgam by Higginbotham and Lapworth (J., 1923, **123**, 1618), who state that "products of at least two distinct types," a volatile β-ketonic ester and a bimolecular compound (III), are formed. No conclusive evidence as to the presence of the β-ketonic ester was given, nor was the dimethylbutanetetracarboxylate isolated, its presence in the primary reduction product being inferred from the production of two isomeric ββ′-dimethyladipic acids by hydrolysis, heating at 160°, and subsequent distillation under low pressure. The author, by employing moist aluminium amalgam as the reducing agent, has found no difficulty in preparing *ethyl dimethylbutanetetracarboxylate* (III) in quantity. On hydrolysis with alcoholic potassium hydroxide, it readily yields a mixture of two stereoisomeric *βγ-dimethylbutane-ααδδ-tetracarboxylic acids*, which can be separated into two forms (*meso* and racemic) melting at 152—154° (decomp.) and 185—185·5° (decomp.), respectively. The racemic configuration is provisionally assigned to the less fusible form. On heating the mixture of the two tetracarboxylic acids at 200°, carbon dioxide was eliminated and a mixture of the two corresponding ββ′-dimethyladipic acids was obtained melting over the range 105—120°, which on esterification and hydrolysis

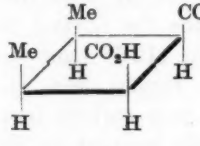
* A description of the application of moist aluminium amalgam in the separation of mixtures of unsaturated compounds, especially those exhibiting three-carbon tautomerism, is reserved for a future communication.

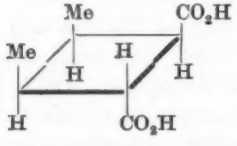
yielded chiefly a mixture of acids, m. p. 113—117° (compare Higginbotham and Lapworth, *loc. cit.*, who found the upper limit of m. p. range was 75° or 128°, according as acetic acid or sodium bicarbonate was used to minimise alkalinity in the sodium amalgam reduction). The description of the separation of the two isomeric ββ′-dimethyladipic acids as well as that of some of their derivatives is reserved for a future paper.

The use of ethyl dimethylbutanetetracarboxylate (III) in synthetical work depends on the fact that it readily yields a *disodium* compound (IV) on treatment with sodium ethoxide or preferably

(IV.) $\begin{matrix}\text{CHMe·CNa(CO}_2\text{Et)}_2\\ \text{CHMe·CNa(CO}_2\text{Et)}_2\end{matrix}$ $\begin{matrix}\text{CHMe—C(CO}_2\text{Et)}_2\\ \text{CHMe—C(CO}_2\text{Et)}_2\end{matrix}$ (V.)

sodium methoxide, the latter being very much more reactive than the former. By bromine, (IV) is quantitatively converted into *ethyl* 2 : 3-*dimethyl*cyclo*butane*-1 : 1 : 4 : 4-*tetracarboxylate* (V). The latter on hydrolysis with alcoholic potash yields the corresponding tetracarboxylic acid, which, on heating to 180°, esterification, and subsequent hydrolysis with alcoholic potassium hydroxide, gives rise to a mixture of the two cyclo*butanedicarboxylic acids* (VI) and (VII), melting respectively at 87—88° and 200·5—201·5°. They

(VI.) 



(VII.)

may be separated by treatment with acetyl chloride (compare Auwers and Thorpe, *Ber.*, 1895, **28**, 623; Komppa, *Annalen*, 1909, **368**, 152; 1909, **370**, 209; Perkin and Scarborough, J., 1921, **119**, 1405); the *trans*-acid remains unaffected whilst the *cis*-acid is converted into the anhydride.

Further evidence in support of ring closure is provided by comparison of the physical properties of the esters (Table I).

TABLE I.

Substance.	B. p.	*d*.	*n*.	$[R_L]$ obs.	$[R_L]$ calc.
$\begin{matrix}\text{MeCH·CH(CO}_2\text{Et)}_2\\ \text{MeCH·CH(CO}_2\text{Et)}_2\end{matrix}$	225—226°/16 mm.	1·0887	1·44873	92·16	91·93
$\begin{matrix}\text{MeCH–C(CO}_2\text{Et)}_2\\ \text{MeCH–C(CO}_2\text{Et)}_2\end{matrix}$ *	208—210°/16 mm.	1·1216	1·45573	90·16	89·73
$\begin{matrix}\text{MeCH·CH}_2\text{·CO}_2\text{Et}\\ \text{MeCH·CH}_2\text{·CO}_2\text{Et}\end{matrix}$	139—141°/15 mm.	0·98777	1·43447	60·74	60·92
$\begin{matrix}\text{MeCH–CH·CO}_2\text{Et}\\ \text{MeCH–CH·CO}_2\text{Et}\end{matrix}$	138—139°/14 mm.	1·00955	1·43888	59·43	58·72

* Slightly impure. See p. 1991.

No details as to temperature, etc., are included, as they are given in full in the experimental section. It is evident that whilst there is no great difference in the boiling points, there are marked differences in the densities and the refractivities, those of the cyclic being greater than those of the corresponding open-chain compounds. The exaltations of the molecular refractivity for the D line of the two *cyclo*butane compounds (0·43 and 0·71) are comparable with those previously observed by other workers for the *cyclo*butane ring (compare Oestling, J., 1912, **101**, 457, mean value 0·48; Eisenlohr, "Spektrochemie organische Verbindungen," 1912, mean value 0·46; Lebedev, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1388, mean value 0·60; Zelinsky, *Ber.*, 1913, **46**, 1093; 1927, **60**, 711, mean value 0·45; Kon, J., 1922, **121**, 513, from *cyclo*hexane*spirocyclo*butanone, 0·77).

The analogous unsubstituted open-chain and *cyclo*butane compounds were prepared many years ago by Perkin (J., 1887, **51**, 1; 1894, **65**, 572). Whilst speculations as to the effect of groups are at present premature—it is hoped to discuss the question fully when a larger number of substituted derivatives have been studied—it may be added that the properties of the $\beta\gamma$-dimethyl homologues are very similar to those of the corresponding unsubstituted compounds, a result which would be expected from the modified strain theory of Thorpe and Ingold, since the normal tetrahedral angle of 115·3° has been altered only to 112·5° (compare Ingold, Sako, and Thorpe, J., 1922, **121**, 1177; Ingold, *ibid.*, p. 2676) by the substitution of CHMe for CH_2. It is a curious fact that the only *cyclo*butanedicarboxylic acid directly isolated by Perkin (*loc. cit.*) was the *cis*-acid, the *trans*-acid being prepared by heating the *cis*-acid with hydrochloric acid at 190°, whereas in the case of the corresponding *cyclo*pentanedicarboxylic acids the *trans*-acid was the only form directly isolated. In the present research, both forms were directly isolated.

The question of the existence of two anhydrides of a *cyclo*butane-1 : 2-dicarboxylic acid is of great interest. Baeyer (*Annalen*, 1890, **258**, 145) predicted from his strain theory that *trans*-anhydride formation should not take place in the *cyclo*propane and should occur in the *cyclo*pentane series, but he was doubtful whether it would be possible in the corresponding 1 : 2-*cyclo*butane-compounds. Perkin (J., 1894, **65**, 572), in testing this prediction experimentally for the unsubstituted *cyclo*butanedicarboxylic acids, found that the *trans*-acid was practically unaffected by heating with acetyl chloride, but on heating with acetic anhydride it was converted into the *cis*-anhydride. The author has found that *trans*-dimethyl-*cyclo*butane-1 : 2-dicarboxylic acid behaves similarly; on heating

it with acetic anhydride for 2 hours, the *cis*-anhydride is produced. It appears that the strain in the *trans*-anhydride is so great that the compound is incapable of isolation under the experimental conditions employed (compare Windaus, Hückel, and Reverey, *Ber.*, 1923, **56**, 91, who have isolated the *trans*-anhydride of hexahydrohomophthalic acid and find that an equilibrium mixture of the *cis*- and *trans*-anhydrides is formed on heating it with acetic anhydride). The question whether the *cis*-anhydride is formed *via* the *cis*-acid or the *trans*-anhydride must still be regarded as an open one.

The ethyl dimethylbutanetetracarboxylate used in this research was obtained by the reduction of ethyl ethylidenemalonate (Goss, Ingold, and Thorpe, J., 1923, **123**, 3353) by moist aluminium amalgam; the yield averaged 45%, the remainder of the product consisting of unchanged malonic ester, which was readily separated by fractional distillation in a vacuum. This yield is surprising, since, under the conditions employed, reduction takes place quantitatively (mesityl oxide, benzylideneacetone) or not at all (ethyl ββ-dimethylacrylate). Two explanations are possible: (*a*) ethyl ethylidenemalonate decomposes under the influence of the moist aluminium amalgam, and (*b*) the ethylidenemalonate contains a considerable quantity of malonic ester which cannot be removed by fractionation in a vacuum. The latter explanation is probably the correct one and receives support from the analytical results as well as from a comparison of the molecular refractivities of Goss, Ingold, and Thorpe's ethyl ethylidenemalonate and that prepared directly from the acid, only the latter exhibiting the expected exaltation due to the presence of conjugated double bonds.

Experimental.

The yield of ethyl ethylidenemalonate, b. p. 113—135°/20 mm., prepared by Goss, Ingold, and Thorpe's method averaged 85 g. from 100 g. of malonic ester [Found: C, 54·5; H, 7·5. Calc. for $CH_3{\cdot}CH{:}C(CO_2Et)_2$: C, 58·1; H, 7·5%. Calc. for $CH_2(CO_2Et)_2$: C, 52·5; H, 7·5%]. On redistillation in a vacuum, a fraction was obtained having b. p. 111—112°/12 mm., $d_4^{17\cdot2}$ 1·05237, $n_D^{17\cdot2}$ 1·42567, $[R_L]_D$ 45·29.

Ethylidenemalonic acid was obtained by adding 50 g. of acetaldehyde to 75 g. of malonic acid in 100 g. of pyridine at −5°, followed by 2·5 c.c. of piperidine during 1 hour, the whole being vigorously stirred. The reaction mixture was kept at 0° overnight, the orange-coloured solid mass cooled to −5° and decomposed with a slight excess of ice-cold dilute sulphuric acid, and the pale yellow ethylidenemalonic acid, m. p. 82° (Komnenos, *Annalen*,

1883, **218**, 165, gives m. p. 84), *quickly* separated. The acid, on esterification with absolute ethyl alcohol and sulphuric acid, yielded ethyl ethylidenemalonate, which was obtained pure after two fractionations in a vacuum. It had b. p. 115—117°/15 mm., $d_4^{17\cdot5^\circ}$ 1·01938, $n_D^{17\cdot5^\circ}$ 1·43007, $[R_L]_D$ 47·17 (calc., 46·60) (compare Komnenos, *loc. cit.*; d^{15° 1·0435) (Found: C, 57·8; H, 7·6. Calc. for $C_9H_{14}O_4$: C, 58·1; H, 7·5%).

Reduction with Moist Aluminium Amalgam. Preparation of Ethyl βγ-*Dimethylbutane*-ααδδ-*tetracarboxylate* (III).—Ethyl ethylidenemalonate (b. p. 113—135°/20 mm.; 150 g.) was reduced by 200 g. of aluminium amalgam prepared by the author's method (this vol., p. 594). The product was worked up in the usual manner and fractionated in a vacuum. Ethyl malonate was recovered below 140°/16 mm.; the temperature then rose rapidly to 210° and *ethyl* βγ-*dimethylbutane*-ααδδ-*tetracarboxylate* distilled at 210—240°/16 mm. (yield, 68 g. or 45%). On refractionation, the pure ester was obtained; it had b. p. 225—226°/16 mm., $d_4^{17\cdot0^\circ}$ 1·0887, $n_D^{17\cdot0^\circ}$ 1·44873, $[R_L]_D$ 92·16 (calc., 91·93) (Found: C, 57·6; H, 8·0. $C_{18}H_{30}O_8$ requires C, 57·8; H, 8·0%). It is a viscid, colourless liquid having a faint odour and on exposure to the atmosphere it slowly becomes pale yellow. The *disodio*-compound (IV) is best prepared from the pure ester and anhydrous sodium methoxide (see below). After being washed with a mixture of pure dry ethyl alcohol and pure dry ether (1 : 3), it is obtained as a pale yellow solid (Found: Na, 11·0. $C_{18}H_{28}O_8Na_2$ requires Na, 11·0%). It decomposes on exposure to the atmosphere.

Hydrolysis of the ester (III). Solutions of the ester (30 g.) in ethyl alcohol (60 g.) and of potassium hydroxide (30 g.) in water (60 g.) were mixed, heated on the steam-bath for 6 hours, and evaporated to dryness. The residue was dissolved in a little water, the solution was extracted with ether to remove any unchanged ester if present and acidified with dilute sulphuric acid, the small quantity of resinous matter which separated was removed by filtration, and the pale yellowish-brown filtrate was saturated with ammonium sulphate and extracted seven times with ether. After *slow* evaporation of the ether, a yellow oil remained which immediately solidified to an almost colourless, crystalline solid (yield, 16 g.), m. p. 155—162° (decomp.). On addition of pure dry ether, the major portion dissolved and a crystalline solid, m. p. 177—179° (decomp.), remained. This was almost pure r-βγ-*dimethylbutane*-ααδδ-*tetracarboxylic acid* (Found: C, 45·6; H, 5·5; equiv., by titration, 66. $C_{10}H_{14}O_8$ requires C, 45·8; H, 5·3%; equiv., 65·5).

Separation of the Two βγ-*Dimethylbutane*-ααδδ-*tetracarboxylic Acids.*—The *r*-acid could be readily isolated from the mixture,

m. p. 155—162° (decomp.) (Found: C, 45·5; H, 5·5%; equiv., by titration, 66), by fractional crystallisation from concentrated hydrochloric acid, in which it was only moderately easily soluble. It was thus obtained in small, hard prisms, m. p. 185—185·5° (decomp.) (Found: C, 45·7; H, 5·4%; equiv., by titration, 66). Other solvents which may be used for the separation are acetone, benzene–alcohol, and ethyl acetate. The *meso*-acid, which is much more soluble than the *r*-acid, can be isolated from the mother-liquors and has m. p. 152—154° (decomp.).

Conversion into a Mixture of ββ′-Dimethyladipic Acids.—Ten g. of the mixture of the tetracarboxylic acids were gradually heated to 200°; the evolution of carbon dioxide then ceased. The whole solidified on cooling to a yellowish-brown mixture (6 g.), m. p. 105—120°, of the two stereoisomeric ββ′-dimethyladipic acids (compare Higginbotham and Lapworth, *loc. cit.*). On esterification with absolute ethyl alcohol and sulphuric acid, the mixed esters, *ethyl ββ′-dimethyladipate*, were obtained. After two fractionations in a vacuum, the liquid had b. p. 139—141°/15 mm., $d_4^{19·5°}$ 0·98777, $n_D^{19·5°}$ 1·43447, $[R_L]_D$ 60·74 (calc., 60·92) (Found: C, 62·4; H, 9·7. $C_{12}H_{22}O_4$ requires C, 62·6; H, 9·6%). It was a mobile liquid with a pleasant ethereal odour. The mixture of esters on hydrolysis with alcoholic potassium hydroxide yielded chiefly a crystalline solid, m. p. 113—117° (Found: equiv., by titration, 89. $C_8H_{14}O_4$ requires equiv., 87).

Synthesis of the cyclo*Butane Ring. Formation of Ethyl* 2 : 3-*Dimethyl*cyclo*butane*-1 : 1 : 4 : 4-*tetracarboxylate* (V).—To 5·3 g. of "molecular" sodium under 200 c.c. of pure dry ether, 15·0 c.c. of pure dry ethyl alcohol were added. When all the sodium had reacted (gentle warming was necessary), a solution of the pure ester (III) (40 g.) in pure dry ether (160 c.c.) was carefully added; the disodio-compound (IV) gradually separated. The mixture was stirred mechanically and dry bromine (5·7 g.) added during 1 hour. The stirring was continued for a further hour, and water then added to dissolve the precipitated sodium bromide. The solution was washed with dilute aqueous sodium bicarbonate and with water and dried with anhydrous sodium sulphate. On evaporation of the ether, a viscid reddish-brown oil (39 g.) was obtained: this was used in all the experiments described below. On fractionation in a vacuum, some carbonisation occurred (compare the corresponding open-chain ester, which distilled unchanged), but most of the liquid distilled as a colourless oil, b. p. 208—210°/16 mm.; this, however, darkened somewhat on exposure to the atmosphere. It had $d_4^{16·7°}$ 1·1216, $n_D^{16·7°}$ 1·45573, $[R_L]_D$ 90·16 (calc., 89·73). Owing probably to the presence of a trace of bromine in the ester, the

analytical results were unsatisfactory (Found: C, 56·4; H, 7·7. $C_{18}H_{28}O_8$ requires C, 58·1; H, 7·5%) (compare Perkin and Robinson, J., 1921, **119**, 1397, who obtained unsatisfactory analytical results for ethyl *cyclo*pentane-1 : 2 : 2 : 3-tetracarboxylate).

It was subsequently found that a much more convenient method of preparation was to use anhydrous sodium methoxide, prepared from "molecular" sodium and pure dry methyl alcohol; the separation of the disodio-compound was then practically complete after 1 hour. The procedure was as described above, the quantities being 6·5 g. of sodium, 11·3 c.c. of methyl alcohol, 250 c.c. of ether; 50 g. of ester in 200 c.c. of ether; and 13·5 c.c. of bromine. The yield of crude *cyclo*butane ester was 49 g. It is not advisable to work with larger quantities, as the yield is thereby materially diminished.

Hydrolysis of the ester (V). Solutions of the ester (50 g.) in alcohol (100 g.) and of potassium hydroxide (50 g.) in water (100 g.) were used. The procedure was that described for the hydrolysis of the ester (III) (p. 1990). The dried ethereal extracts yielded 23 g. of a thick, pale yellow oil—this was employed in all the experiments described below. It slowly crystallised in a vacuum desiccator over concentrated sulphuric acid. The acid separated from ether–light petroleum (b. p. 40—60°) in star-shaped clusters or from benzene–light petroleum in needles, m. p. 138—139° (slight softening at 80°). Correct analytical results for the tetrabasic acid could not be obtained (compare Simonsen, J., 1908, **93**, 1785, who could not obtain correct analytical results for δ-methoxybutane-αα*γγ*-tetracarboxylic acid).

Preparation of a Mixture of the cis- *and* trans-*Forms of* 2 : 3-*Dimethyl*cyclo*butane*-1 : 4-*dicarboxylic Acid*, (VI) *and* (VII).—The tetracarboxylic acid (V) (20 g.) was heated gradually to 180°; the evolution of carbon dioxide then ceased. The gummy residue (compare the ββ′-dimethyladipic acids, which gave a crystalline solid) was esterified with absolute ethyl alcohol and sulphuric acid, and after two fractionations in a vacuum the mixed esters (9·5 g.), *ethyl* 2 : 3-*dimethyl*cyclo*butane*-1 : 4-*dicarboxylate*, were obtained as a fairly mobile liquid with a pleasant ethereal odour and having b. p. 138—139°/14 mm., $d_4^{16·8°}$ 1·00955, $n_D^{16·8°}$ 1·43888, $[R_L]_D$ 59·43 (calc., 58·72) (Found: C, 63·5; H, 8·6. $C_{12}H_{20}O_4$ requires C, 63·2; H, 8·8%). The ester (10 g. in 20 g. of ethyl alcohol) was refluxed with potassium hydroxide (10 g. in 20 g. of water) on the steam-bath for 5 hours. The solution was then evaporated to dryness, the almost colourless residue dissolved in a little water, and the solution extracted with ether, carefully acidified with dilute sulphuric acid, and extracted seven times with ether. The ethereal solution, after being dried with anhydrous sodium sulphate and

evaporated, yielded a colourless oil which immediately crystallised on agitation. On treatment with small quantities of pure dry ether, all the *cis*- and some *trans*-acid dissolved, leaving pure trans-2 : 3-*dimethylcyclobutane*-1 : 4-*dicarboxylic acid*, m. p. 200—201·5°, as a crystalline solid (Found: C, 55·7; H, 7·1; equiv., by titration, 85. $C_8H_{12}O_4$ requires C, 55·9; H, 7·0%; equiv., 86). On evaporation of the ether, a mixture of the *cis*- and *trans*-acids was obtained.

Separation of the cis- *and* trans-*Forms of* 2 : 3-*Dimethylcyclobutane*-1 : 4-*dicarboxylic Acid*.—The mixed acids (2 g.) were warmed to 50° with 4 g. of pure acetyl chloride; a vigorous reaction ensued and hydrogen chloride was evolved. After 1 hour, the liquid mass, containing some suspended crystalline solid (*trans*-acid), was placed in a vacuum desiccator over caustic potash; the excess acetyl chloride was almost wholly removed after 2 days. The semi-solid mass was treated with pure dry ether; some *trans*-acid remained undissolved which, after being washed with small quantities of ether, melted at 200·5—201·5°; the m. p. was unaffected by recrystallisation from acetone–petroleum (b. p. 40—60°). The ethereal solution was washed with dilute aqueous sodium carbonate then with water, and dried with anhydrous sodium sulphate, and the ethereal solution was allowed to evaporate spontaneously. The cis-*anhydride* of 2 : 3-*dimethylcyclobutane*-1 : 4-*dicarboxylic acid* separated in needles, m. p. 50—51° (Found: C, 62·0; H, 6·5. $C_8H_{10}O_3$ requires C, 62·3; H, 6·5%). On acidifying the sodium carbonate washings and repeatedly extracting them with ether, more *trans*-acid was obtained. An aqueous solution of the *cis*-anhydride, on being allowed to concentrate over sulphuric acid, yielded the crystalline cis-*acid*, m. p. 87—88° (Found: C, 55·8; H, 7·0; equiv., by titration, 87. $C_8H_{12}O_4$ requires C, 55·9; H, 7·0%; equiv., 86).

By distilling the mixed acids in a vacuum, the *cis*-acid together with some anhydride, which passes over at a slightly lower temperature, is obtained; this provides the simplest method for the preparation of the pure *cis*-acid or of the *cis*-anhydride.

Attempt to Prepare the Anhydride of trans-2 : 3-*Dimethylcyclobutane*-1 : 4-*dicarboxylic Acid*.—The pure *trans*-acid (1 g.) was gently boiled with an excess of pure redistilled acetic anhydride for 2 hours, and the excess of acetic anhydride removed over caustic potash in a vacuum desiccator. An ethereal solution of the oily residue was washed with dilute aqueous sodium carbonate and with water, dried with anhydrous sodium sulphate, and allowed to evaporate. The *cis*-anhydride, m. p. 50—51°, either alone or when mixed with a specimen prepared from the *cis*-acid, separated in needles.

In conclusion, I wish to thank Professor J. F. Thorpe, F.R.S., for his kind interest and advice. Some of the expenses of the research were met by a grant from the Chemical Society Research Fund.

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CCLXI.—*Chlorocamphoranilic Acids and Camphorochlorophenylimides.*

By MAHAN SINGH and RAM SINGH.

IN a previous communication (J., 1925, **127**, 1966) it was shown that the reaction

$$C_8H_{14}\begin{matrix}CO\cdot NH\cdot C_6H_4R\\CO\cdot OH\end{matrix} \longrightarrow C_8H_{14}\begin{matrix}CO\\CO\end{matrix}N\cdot C_6H_4R + H_2O$$

is dependent on the nature of the group R and other factors, the stability of the acid increasing as R becomes more negative. The carboxycamphoranilic acids (*loc. cit.*) produced by the condensation of camphoric anhydride with aminobenzoic acids are very stable and have not been converted into camphorimides.

The reactions of camphoric anhydride with *o*-, *m*-, and *p*-chloroanilines have now been investigated. The object was to examine the effect of decrease in the negativity of R(CO_2H to Cl) on the above reaction. As expected, the condensation products yielded a mixture of chlorocamphoranilic acids and camphorimide derivatives, thus showing that with the decrease in the negativity of the group there is a tendency towards the formation of ring compounds. The position of the substituent seems to have some effect on the yield of the camphorimide, which is about 20% in the case of the para-derivative and 5 to 6% in the case of the ortho- and meta-derivative. This question is being fully investigated in the condensation products of camphoric anhydride and bromoanilines and iodoanilines.

Wootton (J., 1910, **97**, 405) also has condensed camphoric anhydride with chloroanilines. The melting points of his acids are lower than ours, because they contain the corresponding camphorimides formed in the condensations.

With regard to the optical rotations of the chlorocamphoranilic acids, (*a*) the *o*-chloro-acid gives negative values in acetone and methyl ethyl ketone and positive values in methyl alcohol and ethyl alcohol; (*b*) the relation between the molecular rotation and the position of the chlorine atom is in all solvents $p>m>o$; (*c*) the

molecular rotatory powers of these acids do not follow the order of the dielectric constants of the solvents used.

The following table gives the molecular rotatory powers of camphoranilic acid and some of its ortho-derivatives in methyl alcohol, ethyl alcohol, and acetone.

	$[M]_D$.		
	Methyl alcohol.	Ethyl alcohol.	Acetone.
H*	+150°	+131°	+101°
CO_2H	−584	−574	−551
CH_3*	+146	+144	+ 98
Cl	+ 57·8	+ 35·6	− 40·3

* Singh and Puri, J., 1926, 504.

The relative changes of rotatory power in methyl alcohol and acetone are given by $CO_2H > H > CH_3 > Cl$. This corresponds with the relative polarity of the groups as deduced from molecular inductive capacities (Rule, J., 1926, 553).

The molecular rotations of the *p*- and *m*-substituted camphorophenylimides are considerably lower than those of the corresponding acids, whereas in the case of the *o*-substituted derivatives they are of the same magnitude.

Experimental.

Condensation of Camphoric Anhydride with o-*Chloroaniline.*—Equimolecular quantities of these and a little fused sodium acetate were heated together at 145—150° for 4 hours. The product was dissolved in 90% alcohol, decolorised with animal charcoal, precipitated, and extracted with a dilute solution of sodium bicarbonate, which left a very small residue of camphoro-*o*-chlorophenylimide. This crystallised from alcohol in fine, light needles, m. p. 128° (Wootton, *loc. cit.*, gives m. p. 125—126°). It was soluble in acetone, methyl alcohol, and ether, but sparingly soluble in ethyl alcohol (Found: C, 65·6; H, 6·4; Cl, 12·2. Calc., for $C_{16}H_{18}O_2NCl$: C, 65·8; H, 6·2; Cl, 12·1%).

The bicarbonate solution was acidified and the amorphous solid obtained was recrystallised twice from 60% alcohol; it then melted at 165° (Wootton, *loc. cit.*, gives m. p. 139—140°, which is that of a mixture of 2′-chlorocamphoranilic acid and the imide). *2′-Chlorocamphoranilic acid* is soluble in acetone, methyl alcohol, and ethyl alcohol and moderately easily soluble in ether (Found: C, 62·2; H, 6·8; Cl, 11·2; equiv. by titration with NaOH, 311. $C_{16}H_{20}O_3NCl$ requires C, 62·0; H, 6·5; Cl, 11·5%; equiv., 309·5).

Condensation of Camphoric Anhydride with m-*Chloroaniline.*—The procedure was that described above. The alcoholic solution slowly deposited fine, silky needles of camphoro-*m*-chlorophenyl-

imide, which melted at 176° after recrystallisation (Wootton gives m. p. 172—173°). It was soluble in acetone, methyl alcohol, and ether, and sparingly soluble in ethyl alcohol (Found: C, 66·0; H, 6·9; Cl, 12·2%).

The alcoholic filtrate, on being concentrated, gave a further crop of impure imide. The filtrate from this was poured into a large volume of water, and the precipitate of 3′-chlorocamphoranilic acid thus obtained was dissolved in dilute sodium bicarbonate solution, reprecipitated, and crystallised from 60% alcohol, the pure acid separating in thin plates, m. p. 216—217° (Wootton gives m. p. 207—209°). It was soluble in acetone, methyl alcohol, and ethyl alcohol, and very sparingly soluble in ether (Found: C, 61·8; H, 6·85; Cl, 11·9%, equiv., 304).

Condensation of Camphoric Anhydride with p-*Chloroaniline.*—The procedure was that described above, and the solvent absolute alcohol. The solution slowly deposited stout, prismatic needles of camphoro-*p*-chlorophenylimide, which were twice recrystallised from alcohol; they then melted at 165° (Wootton gives m. p. 162—163°). The imide is soluble in acetone, methyl alcohol and ether, and very sparingly soluble in ethyl alcohol (Found: C, 65·5; H, 6·5; Cl, 12·3%).

From the united filtrates a second crop of the imide was obtained, m. p. 164—165°, after recrystallisation from alcohol. 4′-Chlorocamphoranilic acid, isolated in the same way as the *m*-compound, crystallised from alcohol in needles, m. p. 197° (Wootton gives m. p. 192—194°). It was soluble in acetone, methyl alcohol and ethyl alcohol, and sparingly soluble in ether (Found: C, 61·7; H, 6·6; Cl, 11·9%; equiv., 314).

In all the condensations, complete separation of the acid from the imide could be effected by fractional crystallisation from ethyl alcohol, but it was a rather tedious process.

Molecular rotations of the chlorocamphoranilic acids and camphorochlorophenylimides.

Solvent.	Conc. (g./25 c.c.).	Temp.	α_D.	$[\alpha]_D$.	$[M]_D$.
	2′-Chlorocamphoranilic acid.				
MeOH	0·4391	18°	+0·61°	+18·7°	+57·8°
EtOH	0·4444	,,	+0·41	+11·5	+35·6
Me_2CO	0·2654	,,	−0·28	−13·2	−40·8
MeEtCO	0·4210	,,	−0·29	− 8·6	−26·6
	3′-Chlorocamphoranilic acid.				
MeOH	0·1475	18	+0·62	+52·5	+162·4
EtOH	0·1384	,,	0·48	43·3	134·0
Me_2CO	0·1268	,,	0·32	31·5	97·5
MeEtCO	0·1306	,,	0·42	40·2	124·4

Solvent.	Conc. (g./25 c.c.).	Temp.	α_D.	$[\alpha_D]$.	$[M]_D$.
		4′-Chlorocamphoranilic acid.			
MeOH	0·1870	18°	+0·88	+58·8	+183·0
EtOH	0·1314	,,	0·54	51·3	158·7
Me_2CO	0·1493	,,	0·46	38·5	119·0
MeEtCO	0·1302	,,	0·51	48·9	150·3
		Camphoro-*o*-chlorophenylimide.			
MeOH	0·1522	25°	+0·16	+13·14	+38·3
EtOH	0·1592	,,	0·18	14·1	41·1
Me_2CO	0·2468	,,	0·24	12·1	35·2
MeEtCO	0·2348	,,	0·26	13·8	40·2
		Camphoro-*m*-chlorophenylimide.			
MeOH	0·2030	25°	+0·23	+14·16	+41·1
EtOH	0·2256	,,	0·25	13·8	40·2
		Camphoro-*p*-chlorophenylimide.			
MeOH	0·2014	25°	+0·32	+19·8	+51·7
EtOH	0·2589	,,	0·33	15·9	46·4
Me_2CO	0·2432	,,	0·28	14·3	41·7
MeEtCO	0·3326	,,	0·44	16·5	48·0

The readings were taken in a 2-dm. tube within ½ hour of making up the solution. There was no mutarotation.

We desire to thank Dr. H. B. Dunnicliff for his kindly interest in this work.

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CCLXII.—δ-d-*Bornylsemicarbazide and* δ-d-neo*Bornylsemicarbazide.*

By JOHN AUGUSTUS GOODSON.

FOR an investigation, which has so far given negative results, the author has had occasion to prepare a quantity of δ-*d*-bornylsemicarbazide and δ-*d*-*neo*bornylsemicarbazide. The use of such optically active semicarbazides for the resolution of racemic carbonyl compounds has been suggested by various workers and a number of them have been prepared, *e.g.*, camphoryl-ψ-semicarbazide (Forster and Fierz, J., 1905, **87**, 722), δ-α-phenylethylsemicarbazide (Wilson, Hopper, and Crawford, J., 1922, **121**, 866), and δ-menthylsemicarbazide (Wilson and Crawford, J., 1925, **127**, 103), whilst Forster and Attwell attempted to prepare β-bornylsemicarbazide (J., 1904, **85**, 1188), but in no case have these substances so far been used successfully for this purpose. δ-*d*-Bornylsemicarbazide

and δ-*d*-*neo*bornylsemicarbazide were only tried on one racemic ketone, *viz.*, 3-methyl*cyclo*hexanone, and although well-crystallised products were obtained, they did not separate into optical antipodes on fractional crystallisation from two solvents.

EXPERIMENTAL.

Acetone-δ-d-*bornylsemicarbazone*.—To *d*-bornylamine (10 g.) melted by immersion in an oil-bath at 175°, was added acetone-semicarbazone (7·5 g.) a little at a time, and the heating continued for 15 minutes. The cold crystalline product was recrystallised from alcohol, and active *acetone*-δ-d-*bornylsemicarbazone* obtained in anhydrous needles (yield, 76%), m. p. 141—148° (corr.), $[\alpha]_D^{20°}$ + 25·5° (c = 2·04 in dry alcohol) (Found : C, 66·7; H, 10·0; N, 16·5. $C_{14}H_{25}ON_3$ requires C, 66·9; H, 10·0; N, 16·7%).

In order to obtain a good yield, it is necessary to use anhydrous *d*-bornylamine. In a preliminary experiment, *d*-bornylamine containing two molecules of water of crystallisation, obtained by precipitation with sodium hydroxide from a solution of the hydrochloride, was used; a considerable quantity of di-*d*-bornylcarbamide was then produced.

δ-d-*Bornylsemicarbazide Hydrochloride*.—Acetone-δ-*d*-bornylsemicarbazone (85 g.) and 10% hydrochloric acid (850 c.c.) were heated on the water-bath for 1½ hours. δ-*Bornylsemicarbazide hydrochloride* crystallised on cooling and was recrystallised from alcohol after removal of a small quantity of di-*d*-bornylcarbamide by filtration (yield, 94%). The anhydrous substance, m. p. 190—198° (corr.), had $[\alpha]_D^{20°}$ + 2·6° (c = 5 in dry alcohol) (Found in air-dried substance : loss at 105° in a vacuum, 14·1. $C_{11}H_{22}ON_3Cl,2H_2O$ requires H_2O, 12·7%. Found in anhydrous substance : C, 53·1; H, 8·9; Cl, 14·2. $C_{11}H_{22}ON_3Cl$ requires C, 53·3; H, 9·0; Cl, 14·3%).

δ-d-*Bornylsemicarbazide*.—δ-*d*-Bornylsemicarbazide hydrochloride (10 g.) dissolved in a little alcohol was treated with 8·5 c.c. of 20% sodium hydroxide solution and poured into water. The base was extracted with chloroform and obtained in needles by addition of light petroleum to the concentrated solution. The substance, dried in a vacuum at 50°, melted at 75° after softening some degrees lower, and had $[\alpha]_D^{20°}$ + 17·0° (c = 5 in dry alcohol). On keeping, it gradually decomposed (Found in dried substance : C, 62·5; H, 10·4. $C_{11}H_{21}ON_3$ requires C, 62·5; H, 10·0%).

δ-*d*-Bornylsemicarbazones of various ketones were prepared by adding the requisite quantity of ketone to a concentrated solution of the base in alcohol.

iso*Pulegone*-δ-d-*bornylsemicarbazone*, prepared from *iso*pulegone

having $\alpha_D^{18°} - 6{\cdot}0°$, crystallised in thick, rhombic plates, m. p. 224—226° (corr.), $[\alpha]_D^{20°} + 9{\cdot}2°$ ($c = 5{\cdot}04$ in chloroform) (Found: C, 72·8; H, 10·1. $C_{21}H_{35}ON_3$ requires C, 73·0; H, 10·2%).

4-*Methyl*cyclo*hexanone*-δ-d-*bornylsemicarbazone* crystallised in clusters of six-sided plates, softening slightly at 145° (corr.), melting at 154° (corr.), and having $[\alpha]_D^{20°} + 27{\cdot}2°$ ($c = 4{\cdot}898$ in dry alcohol) (Found: C, 70·5; H, 10·2. $C_{18}H_{31}ON_3$ requires C, 70·8; H, 10·2%).

3-*Methyl*cyclo*hexanone*-δ-d-*bornylsemicarbazone*, prepared from optically inactive 3-methyl*cyclo*hexanone, melted at 172—177° (corr.) and had $[\alpha]_D^{20°} + 27{\cdot}4°$ ($c = 4{\cdot}85$ in dry alcohol) (Found: C, 70·5; H, 10·1. $C_{18}H_{31}ON_3$ requires C, 70·8; H, 10·2%). Recrystallisation from alcohol or ligroin failed to resolve it into its components, even when seeded with d-3-*methyl*cyclo*hexanone*-δ-d-*bornylsemicarbazone*, m. p. 173—179° (corr.), $[\alpha]_D^{20°} + 7{\cdot}4°$ ($c = 4{\cdot}726$ in dry alcohol) (Found: C, 70·4; H, 10·1. $C_{18}H_{31}ON_3$ requires C, 70·8; H, 10·2%), prepared from *d*-3-methyl*cyclo*hexanone kindly supplied by Dr. Kenyon.

Acetone-δ-d-neo*bornylsemicarbazone*, prepared in the same way as acetone-δ-*d*-bornylsemicarbazone, but at 190° in order to keep the *neo*bornylamine liquid, crystallised from alcohol in anhydrous needles, m. p. 175—179° (corr.), $[\alpha]_D^{20°} - 92{\cdot}1°$ ($c = 2{\cdot}008$ in dry alcohol) (Found: C, 66·6; H, 10·1. $C_{14}H_{25}ON_3$ requires C, 66·9; H, 10·0%).

δ-d-neo*Bornylsemicarbazide hydrochloride* was prepared by hydrolysis of the above acetone derivative with dilute hydrochloric acid. The anhydrous substance melted at 198—202° (corr.) and had $[\alpha]_D^{20°} - 50{\cdot}8°$ ($c = 4{\cdot}982$ in dry alcohol) (Found in air-dried substance: loss at 105° in a vacuum, 5·3. $C_{11}H_{22}ON_3Cl,H_2O$ requires H_2O, 6·8%. Found in substance dried at 105° in a vacuum: Cl, 14·1. $C_{11}H_{22}ON_3Cl$ requires Cl, 14·3%).

δ-*d*-*neo*Bornylsemicarbazones were prepared by adding the requisite quantity of ketone to a concentrated solution of δ-*d*-*neo*-bornylsemicarbazide in alcohol.

4-*Methyl*cyclo*hexanone*-δ-d-neo*bornylsemicarbazone* crystallised in rosettes of needles, m. p. 151—155° (corr.), $[\alpha]_D^{20°} - 91{\cdot}3°$ ($c = 2{\cdot}83$ in dry alcohol) (Found: C, 70·4; H, 10·0. $C_{18}H_{31}ON_3$ requires C, 70·8; H, 10·2%).

3-*Methyl*cyclo*hexanone*-δ-d-neo*bornylsemicarbazone*, prepared from optically inactive 3-methyl*cyclo*hexanone, melted at 157—161° (corr.) and had $[\alpha]_D^{20°} - 91{\cdot}2°$ ($c = 4{\cdot}772$ in dry alcohol) (Found: C, 70·6; H, 10·3. $C_{18}H_{31}ON_3$ requires C, 70·8; H, 10·2). Recrystallisation from alcohol or ligroin failed to resolve it into its components.

The author desires to express his thanks to Mr. R. E. Hedger for assistance in the work and to Dr. Kenyon for supplying the *d*-3-methyl*cyclo*hexanone used.

WELLCOME CHEMICAL RESEARCH LABORATORIES.

[*Received, July 16th*, 1927.]

CCLXIII.—*The Absorption Spectrum of Ergosterol in Relation to the Photosynthetic Formation of Vitamin* D.

By RICHARD ALAN MORTON, ISIDOR MORRIS HEILBRON, and EDWARD DAVID KAMM.

IT has been shown (Heilbron, Kamm, and Morton, *Biochem. J.*, 1927, **21**, 78) that the antirachitic potency developed on irradiation of ordinary cholesterol, either from cod-liver oil or from brain, may be traced to the presence in it of a minute quantity of some foreign substance which exhibits well-defined absorption bands near 293·5 μμ, 281·5 μμ, and 270 μμ. These bands disappear on irradiation, concomitantly with the development of antirachitic potency in the product. A similar conclusion was almost simultaneously arrived at by Pohl (*Nach. Ges. Wiss. Göttingen*, 1926), using an entirely different spectroscopic technique (monochromatic light and photo-electric cells). These results are also substantiated by the fact that cholesterol regenerated from its dibromide could not be activated by irradiation with ultra-violet light. Subsequent work developed by using the spectroscopic method rapidly led to the conclusion that ergosterol—or a similar sterol—is the actual pro-vitamin, and this has been fully substantiated by animal tests (Rosenheim and Webster, *Biochem. J.*, 1927, **21**, 127; Windaus and Hess, *Nach. Ges. Wiss. Göttingen*, 1926).

In extension of our earlier work, it became necessary to examine in detail the absorption spectrum of ergosterol, in order to establish an accurate standard of comparison by means of which we could determine the relative richness of various materials in respect of the pro-vitamin.

In agreement with the work of Pohl as briefly reported by Windaus and Hess (*loc. cit.*), our results correspond in a very remarkable degree with the absorption curve found for ordinary cholesterol:

	λ max.	λ max.	λ max.
Cholesterol	293 μμ	280 μμ	269 μμ
Ergosterol	293·5 μμ	281·5 μμ	270 μμ

Further, the results indicate that ergosterol is 2—4 × 10^3 times as active as our specially prepared cholesterol (Heilbron, Kamm, and Morton, *loc. cit.*).

We next studied the change in the absorption spectrum brought about by irradiation of ergosterol in alcoholic solution. A solution of 0·05 g. of ergosterol in 250 c.c. of optically pure alcohol was prepared and portions were exposed to the light of a practically *new* (Hewittic) quartz mercury-vapour lamp of the vacuum type. Samples were withdrawn every 15 minutes and the absorption spectrum was determined. For this purpose two Hilger E_3 quartz spectrographs were used alternately, each being fitted with a rotating disc sector photometer. Two series of absorption curves were obtained showing the selective absorption at half-hour intervals. The two sets of curves were reasonably concordant and only one will therefore be described.

1. Ergosterol. Fresh solution not irradiated. Bands at 270 μμ, 281·5 μμ, and 293·5 μμ. Minimum 230 μμ. "ε" max. 10,200. "ε" min. 2,400.

2. Irradiated for 30 minutes. Broad maximum near 275 μμ. "ε" max. 8,500. Minimum near 230 μμ. "ε" min. 3,750. The absorption band is wider in the region 230—265 μμ than the corresponding band for the fresh solution.

3. Irradiated for 60 minutes. Broad maximum near 275 μμ. "ε" max. 7,150. Minimum near 230 μμ. "ε" min. 4,850. The curve shows a marked step-out in the region 240—260 μμ, indicating the incipient appearance of a band in that region of the spectrum.

4. Irradiated for 90 minutes. The curve shows a new maximum near 247 μμ. "ε" max. 6,300 and a minimum near 230 μμ. "ε" min. 5,800. The persistence of the new band is therefore low. At the same time the absorption curve shows marked absorption over the region 260—300 μμ, indicating that the ergosterol has not entirely disappeared.

5. Irradiated for 120 minutes. The band at 247 μμ has increased in persistence, whilst the absorption over the range 260—300 μμ shows a collateral decrease.

6. Irradiated 150 minutes. The band at 247 μμ is well developed. "ε" max. 5,250, a minimum is shown at 225 μμ, and the persistence is considerable. From 247 μμ—269 μμ the absorption curve is fairly straight, but at 270 μμ a sharp inflexion commences and the curve falls slowly to the limiting position near 310 μμ.

7. Irradiated for 6 hours. The solution is now almost diactinic and all trace of selective absorption has disappeared.

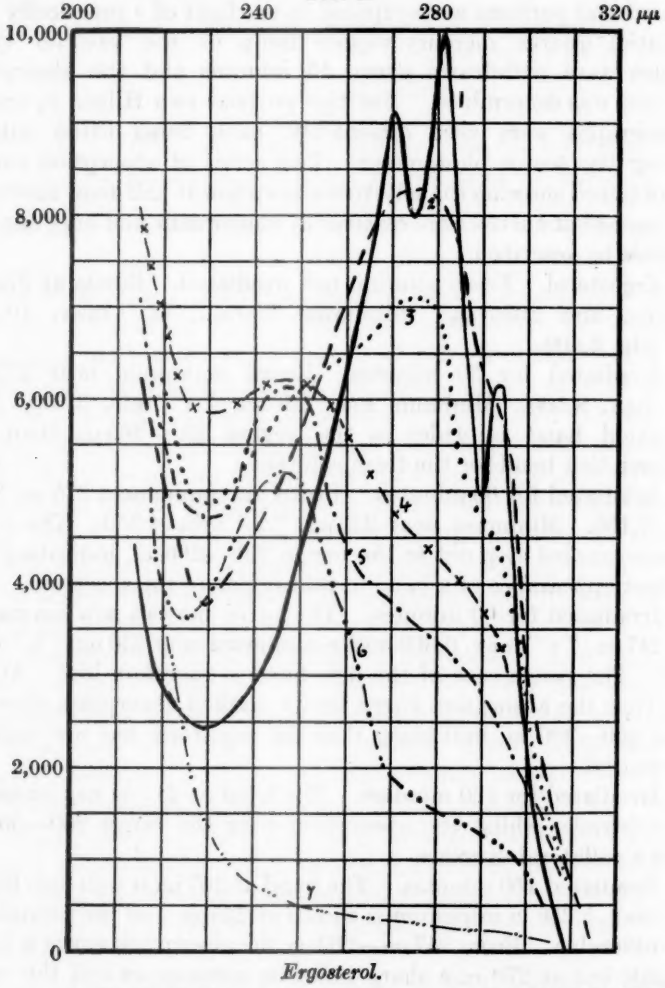
The curves (Fig. 1) show that the reaction

$$\text{ergosterol} \xrightarrow{\text{u.v. light}} \text{vitamin } D \quad . \quad . \quad . \quad . \quad (1)$$

is accompanied by the disappearance of selective absorption in the region 260—300 μμ and by the appearance of a new selective absorp-

tion in the region 230—260 $\mu\mu$ with a maximum at 247 $\mu\mu$. This new band itself disappears with further irradiation, a fact which is

FIG. 1.



Ergosterol.

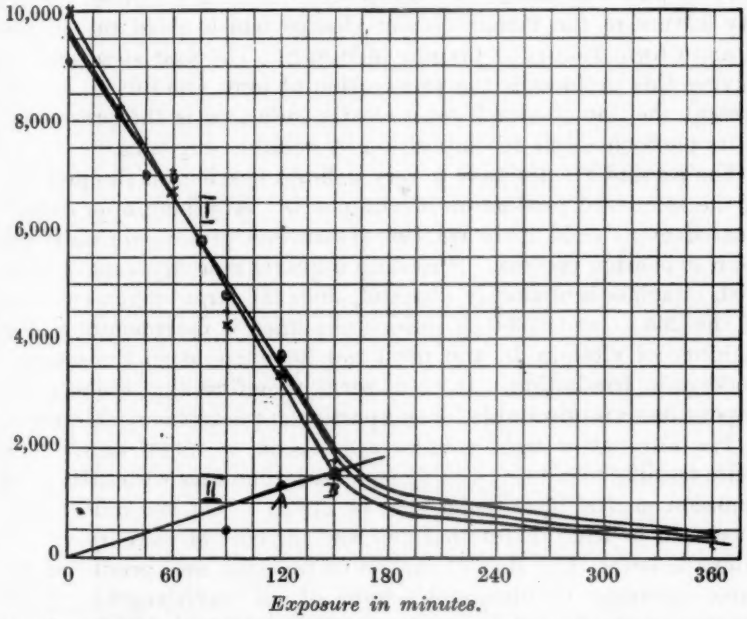
1 ————	*Fresh solution.*	5 —·—·—·	*Irradiated for* 120 *mins*
2 · · · · · ·	*Irradiated for* 30 *mins.*	6 —··—··—	,, ,, 150 ,,
3 · · · · · ·	,, ,, 60 ,,	7 —···—···—	,, ,, 6 *hrs.*
4 —×—×—	,, ,, 90 ,,		

not inconsistent with the view that it is due to vitamin *D*, since it is known that "excessive" irradiation of cod-liver oil induces a loss of vitamin potency.*

* The results of biological experiments have now come to hand and show that the product giving the 247 $\mu\mu$ band at maximum intensity possesses very

When the extinctions at 270—275 μμ and 280 μμ are plotted against time, the result is, within experimental error, a straight line, indicating that the rate of disappearance of ergosterol depends solely on the energy input. By plotting the persistence of the new band against time, a roughly linear relation is likewise obtained (Fig. 2). These results can only mean that the *whole* of the incident energy is absorbed and is photochemically effective, within the absorption band and within the limits of the straight line relationship.

FIG. 2.



I, *extinction coefficients at* 281·5 μμ, 275 μμ, 270 μμ, *ergosterol curves.*
II, *persistence of new band* (*line* AB *produced cuts axes at origin*).

In our experience, the irradiation of thin layers of solid ergosterol is unsatisfactory. Complete disappearance of the original bands is secured only after long exposure and under conditions in which consecutive reactions are not precluded.

The absorption curves indicate a fact of considerable significance, namely, that the irradiation of ergosterol in solution or in the solid state is quite unlikely to give pure vitamin *D* unless special precautions are taken. The existence of a well-marked absorption

high antirachitic potency, whereas the product which has undergone irradiation until this band has disappeared is not effective at the same dosage. The tests were kindly carried out by Messrs. H. Jephcott and A. L. Bacharach, using the method described in their paper (*Biochem. J.*, 1926, **20**, 1351).

band between 225 μμ and 270 μμ characteristic of a photochemically unstable substance, *viz.*, vitamin *D*, means that if photodecomposition of this compound is to be avoided, *these radiations must be screened off*. The most suitable material for transmitting only light of the middle ultra-violet region is the proprietary "Vitaglass." Since, however, the rays between 270 and 293 μμ are absorbed to a considerable extent by vitaglass, very prolonged exposures will be necessary. Rosenheim and Webster (*Biochem. J.*, 1927, **21**, 392) state that "the action of ultra-violet light on ergosterol leads to an obvious physical change and the production of a yellowish resin." The nature of the intramolecular change which gives rise to the vitamin formation is at present unknown. The first step towards solving this problem is the preparation of pure vitamin *D*, and at present the line of attack most clearly indicated is the prevention of its photochemical decomposition by suitable screening.

The present results have a very definite bearing on the problem of the industrial production of vitamin *D*. Anything approaching a satisfactory yield in the reaction (1) requires prolonged irradiation —an expensive process. Screening a quartz mercury-vapour lamp with vitaglass is obviously wasteful, since the large energy emission of the 265 μμ and 253·6 μμ (resonance) lines is detrimental to the stability of vitamin *D*, and must not have access to the solution undergoing irradiation. It would seem, therefore, that the mercury vapour lamp is unsuitable for this particular photochemical reaction.

The alternative light sources are carbon or metal arcs. It is quite feasible to obtain suitably treated carbon arcs with little or no emission on the ultra-violet side of 270 μμ. On the other hand, there can be little doubt that the working cost of mercury vapour lamps is lower than that of carbon or tungsten arcs producing the same intensity of ultra-violet light of all wave-lengths. These considerations show that the photochemical formation of vitamin *D* in good yield presents a formidable problem both to research and to costing. There seems, however, every reason to expect a solution if the experiments are accurately controlled by spectroscopic means.

Some comment is necessary on a statement by Rosenheim and Webster (*Biochem. J.*, 1927, **21**, 395) to the effect that the absorption of ergosterol "extends well into the ultra-violet region of sunlight." The facts appear to be as follows. Dorno found that the limiting detectable ultra-violet wave-lengths of sunlight were: December—February, 3120 Å.; September—November, 3080 Å.; March—May, 3010 Å.; June—August, 2962 Å.; the relative intensities being Jan. 100, April 400, July 1000, October 600.

Only a very small area of the ergosterol absorption is covered by wave-lengths on the long-wave side of 2960 Å., and appreciable

photochemical reaction only appears possible in summer sunlight. This is, of course, in harmony with the seasonal incidence of rickets.

A brief remark on the paper by Hume, Lucas, and Smith (*Biochem. J.*, 1927, **21**, 362) is also necessary. These authors suggest that the mechanism of synthesis of vitamin *D in vivo* is the photochemical transformation of traces of ergosterol or a substance with similar absorption bands. Unfortunately, the transmission of epidermis falls to zero near 296 $\mu\mu$, so that a direct experimental test is excluded. We propose to investigate the matter further in two ways :

(1) To ascertain spectroscopically whether ergosterol, in solution in a quartz vessel, can be transformed into vitamin *D* by exposure to sunlight.

(2) To ascertain whether an extract containing ergosterol can be prepared from skin by means of solvents.

During the course of this work preliminary attempts were made to ascertain whether the formation of vitamin *D* is due to polymerisation. Determinations of molecular weight by the Rast micro-method failed to establish any such change, but we were not completely satisfied with the conditions under which the determinations were carried out and are repeating and extending the experiments.*

We desire to express our thanks to Mr. W. Doran and Mr. M. N. Leathwood for help in the experimental work, to Mr. F. H. Carr, C.B.E., of British Drug Houses, Ltd., for the ergosterol, and to the Food Investigation Board for a grant which has enabled this research to be carried out.

THE UNIVERSITY, LIVERPOOL. [*Received, May 27th*, 1927.]

CCLXIV.—*Studies in the Coumarin Series. Part I. The Action of the Grignard Reagent upon Substituted Coumarins.*

By ISIDOR MORRIS HEILBRON and DOUGLAS WILLIAM HILL.

DECKER and FELLENBERG (*Annalen*, 1907, **356**, 281) have shown that the interaction of coumarins and the Grignard reagent leads, under carefully specified conditions, to the production of mono-alkyl- or -aryl-pyrylium salts, and more recently Willstätter and his

* Whilst this paper was in the press, our attention was drawn to a paper by Pohl (*Nach. Ges. Wiss. Göttingen*, Mathematisch-Physikalische Klasse, 1927) in which the absorption curves of ergosterol and vitamin *D* are described. The photoelectric and photographic methods are in substantial agreement.

co-workers (*Ber.*, 1924, **57**, 1938, 1945) have used this reaction for the synthesis of anthocyanidins from 3-methoxycoumarins. On the other hand, Houben (*Ber.*, 1904, **37**, 498) has described the formation of dialkyl and diaryl derivatives of coumarin itself. Whereas magnesium alkyl halides led to the formation of 2 : 2-dialkyl-Δ^3-chromens, magnesium phenyl bromide gave rise to the carbinol (I), the formation of which he attributed to a steric hindrance preventing the loss of water necessary for the production of the 2 : 2-diphenylchromen.

The work described in the present paper was initially undertaken with the intention of synthesising flavylium chlorides containing methoxyl or hydroxyl in the 4-position; the latter would probably readily lose hydrogen chloride and pass into flavones. As, however, only diaryl products were obtained, a detailed investigation of coumarins substituted in the 3- and 4-positions was initiated which has led to the isolation of three distinct types of product. Two of these, differently constituted diarylchromens, are now described; the third, a series of benzopyrylium salts, will form the subject of a subsequent communication. While this work was in progress, a most noteworthy contribution to the subject was published by Löwenbein (*Ber.*, 1924, **57**, 1517), who showed that the supposed diphenyl-*o*-hydroxystyrylcarbinol (I) of Houben is in reality 2 : 4-diphenylchroman-2-ol (II), which readily loses water on heating with glacial acetic acid, yielding 2 : 4-diphenyl-Δ^2-chromen (III).

(I.) $C_6H_4\langle^{CH:CH\cdot CPh_2\cdot OH}_{OH}$ $\qquad$ $C_6H_4\langle^{CHPh\cdot CH_2}_{O\text{——}CPh\cdot OH}$ (II.)

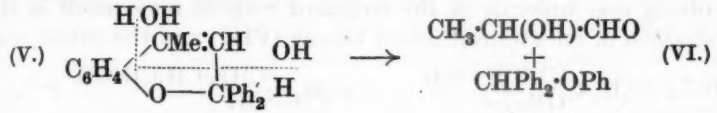
In addition to the chromanol, he obtained a second compound which proved to be 2 : 2-diphenyl-Δ^3-chromen (IV).

(III.) $C_6H_4\langle^{CHPh\cdot CH}_{O\text{——}CPh}$ $\qquad$ $C_6H_4\langle^{CH:CH}_{O\text{—}CPh_2}$ (IV.)

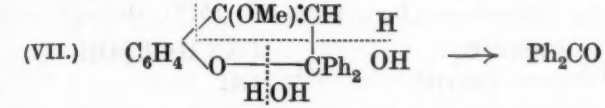
Löwenbein also examined the 5 : 7-, 4 : 6-, and 4 : 7-dimethylcoumarins, all of which, according to him, yielded the corresponding chromanols analogous to (II).

In the course of our own experiments, the action of magnesium phenyl bromide upon both 3-methyl- and 3-phenyl-coumarin was studied. In each case the corresponding chromanol was isolated, from which the elements of water were readily eliminated on heating with glacial acetic acid, 2 : 4-diphenyl-3-methyl-Δ^2-chromen and 2 : 3 : 4-triphenyl-Δ^2-chromen, respectively, being formed. Since these compounds were prepared, a full description of the latter has been published by Löwenbein and Rosenbaum (*Annalen*, 1926, **448**, 223), who have prepared it both from 3-phenylcoumarin and

by the interaction of magnesium phenyl bromide upon 2 : 3-diphenylbenzopyrylium perchlorate.*



On the other hand, 4-methyl- and 4-methoxy-coumarins yield 2 : 2-*diphenyl*-4-*methyl*-Δ^3-*chromen* (V) and 4-*methoxy*-2 : 2-*diphenyl*-Δ^3-*chromen* (VII), respectively.



According to Löwenbein (*loc. cit.*), certain Δ^3-chromens are converted into coumarone derivatives of the same empirical formula on boiling with glacial acetic acid. Neither of the above compounds (V and VII) was altered under such conditions. That, however, they are in reality Δ^3-chromens has been definitely established by a study of their products of hydrolysis. 2 : 2-Diphenyl-4-methyl-Δ^3-chromen was refluxed for 24 hours with 50% potassium hydroxide solution; ring scission then occurred with production of *benzhydryl phenyl ether* (VI). With 4-methoxy-2 : 2-diphenyl-Δ^3-chromen, refluxing for 5 hours with 33% potassium hydroxide solution was sufficient to cause complete scission. The product isolated in this case was benzophenone, cleavage occurring in the same manner as found by Baker (J., 1925, **127**, 2349). These results, although not wholly in agreement with Löwenbein's findings in the case of the 4 : 6- and 4 : 7-dimethylcoumarins, harmonise well with the work of Kohler (*Amer. Chem. J.*, 1907, **38**, 511), who has shown that addition of the Grignard reagent to $\alpha\beta$-unsaturated ketones takes place both in the 1 : 2 and in the 1 : 4 positions, the relative amounts of each compound formed being dependent on the nature of the unsaturated compound; *e.g.*, the unsaturated ketone $C_6H_5{\cdot}CH{:}CH{\cdot}CO{\cdot}C_6H_5$ gives mainly 1 : 4 addition (94—96%), whereas $(C_6H_5)_2C{:}CH{\cdot}CO{\cdot}C_6H_5$ yields 100% of unsaturated alcohol owing to complete 1 : 2 addition.

Our experiments with coumarins have led us to the definite conclusion that the primary reactions with the Grignard reagent follow a common course, the ultimate formation of a Δ^2- or Δ^3-chromen being influenced solely by the position of the substituent

* Dr. Löwenbein informs me (private communication) that he has also prepared 2 : 4-diphenyl-3-methyl-Δ^3-chromen (m. p. 94°) by the decomposition of 2-phenyl-3-methylbenzopyrylium perchlorate with magnesium phenyl bromide—I. M. H.

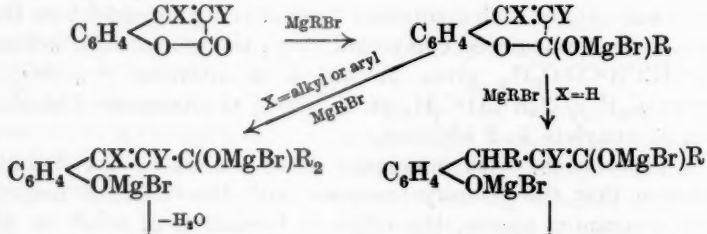
in the pyran ring. Two explanations may be presented to meet the above postulation. In the first place, the primary reaction involving one molecule of the Grignard reagent may result in the production of an αβ-unsaturated ketone (VIII) and the subsequent

(VIII.) $C_6H_4<^{CX:CH\cdot COR}_{OMgBr}$ $C_6H_4<^{CHR\cdot CH:CR\cdot OH}_{OH}$ (IX.)

reactions would then directly follow the Kohler rule. Where X = hydrogen, 1 : 4 addition would chiefly occur with production of the enol (IX), from which the chromanol (X) would result, as pointed out by Löwenbein (*Ber.*, 1924, **57**, 1517), through intra-

(X.) $C_6H_4<^{CHR\cdot CH_2}_{O\text{——}CR\cdot OH}$ $C_6H_4<^{CX:CH\cdot CR_2\cdot OH}_{OH}$ (XI.)

molecular rearrangement from the keto-form. On the other hand, where X is other than hydrogen, 1 : 2 addition will take place, giving the styrylcarbinol (XI), which will immediately pass into the Δ^3-chromen by loss of a molecule of water. Löwenbein considers, however, that Δ^3-chromen formation occurs directly without opening of the lactone ring, since phenyl *o*-hydroxystyryl ketone yields only 2 : 4-diphenylchroman-2-ol when treated with magnesium phenyl bromide, whereas, as previously mentioned, coumarin gives both the chromanol and the Δ^3-chromen. It will be conceded, however, that the reactions involved with the two compounds are not identical and that the presence of the free *o*-hydroxyl group in the ketone may well favourably influence the 1 : 4 addition. An alternative mechanism differing only in degree from the above, and equally explicable on the Kohler rule, may also be reached by assuming that the first reaction with the Grignard reagent comprises direct addition without ring opening. The course of the subsequent reactions under these conditions is expressed by the following formulæ :

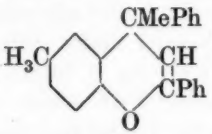


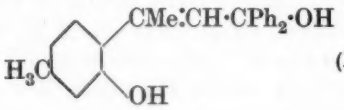
Either explanation provides a perfectly general interpretation of the Δ^2- or Δ^3-diarylchromen formation and meets the problem presented by the 3-substituted coumarins which fail to yield

Δ^3-diarylchromens, a result incompatible with the idea that interaction can occur directly without scission of the lactone ring. The fact that whereas coumarin itself gives both the 1 : 4- and 1 : 2-addition products, whilst the 3-substituted coumarins give only 1 : 4-addition, is also in agreement with Kohler's findings in the case of the unsaturated ketones $C_6H_5 \cdot CH{:}CMe \cdot CO \cdot C_6H_5$ and $C_6H_5 \cdot CH{:}CPh \cdot CO \cdot C_6H_5$.

The complete harmony between our experimental results and these theoretical deductions induced us to re-examine the products obtained from both 4 : 6- and 4 : 7-dimethylcoumarin, which, according to Löwenbein, yielded 2 : 4-diphenylchroman-2-ol derivatives. Working in exact accordance with this author's conditions, we failed to obtain from 4 : 6-dimethylcoumarin any trace of the so-called chromanol, m. p. 110°, but isolated in good yield a substance, m. p. 127°, which corresponded to the compound obtained by Löwenbein by treatment of the chromanol with glacial acetic acid and to which he assigned the structure of 2 : 4-diphenyl-4 : 6-dimethyl-Δ^2-chromen (XII). The main yield from 4 : 7-dimethylcoumarin was a compound, m. p. 86°, apparently identical with the supposed 2 : 4-diphenyl-4 : 7-dimethyl-Δ^2-chromen (m. p. 87°). In addition, a very small yield of a substance, m. p. 146°, was obtained of empirical formula $C_{23}H_{22}O_2$, corresponding to the supposed 2 : 4-diphenyl-4 : 7-dimethylchroman-2-ol of m. p. 144°.

(XII.)





(XIII.)

The fact that chromens were obtained directly from the products of the reaction is in itself some indication that these do not belong to the Δ^2-series, and this we have proved by an examination of their scission products. Benzhydryl *p*-tolyl ether was obtained in good yield from the 4 : 6-dimethyl compound. In the case of 2 : 2-diphenyl-4 : 7-dimethyl-Δ^3-chromen, in addition to benzhydryl *m*-tolyl ether, lactaldehyde, m. p. 105°, was isolated, thus definitely establishing the constitution of these compounds as diaryl-Δ^3-chromens.

The substance, m. p. 146°, is probably the intermediate *diphenyl-2-hydroxy-*β : *4-dimethylstyrylcarbinol* (XIII), but the quantity at our disposal did not allow of detailed examination.

We acknowledge our indebtedness to Dr. A. Löwenbein, with whom we have been in communication concerning the mechanism of the changes involved in these reactions, and who has freely given us the advantage of his views.

EXPERIMENTAL.

4-Hydroxy-2 : 2-diphenyl-Δ^3-chromen.—Magnesium phenyl bromide (prepared from bromobenzene, 14·5 g., magnesium turnings, 2·5 g., and ether, 100 c.c.) was added to 4-hydroxycoumarin (5 g.), suspended in benzene (250 c.c.). A solid was rapidly precipitated which did not redissolve after 5 hours' heating under reflux. The reaction mixture was decomposed by ice-cold, dilute hydrochloric acid, unchanged bromobenzene and diphenyl were removed by steam distillation, and the residual solid was separated from unacted-upon 4-hydroxycoumarin by boiling with water, in which the latter was readily soluble. After drying, the *chromen* was crystallised from benzene and then twice from absolute alcohol, from which it separated in colourless needles, m. p. 230—231°. It is strongly acidic and dissolves readily in sodium hydroxide and sodium carbonate solutions; it gives no coloration with ferric chloride (Found: C, 83·9; H, 5·1. $C_{21}H_{16}O_2$ requires C, 84·0; H, 5·3%).

4-Methoxy-2 : 2-diphenyl-Δ^3-chromen (VII).—This was prepared in an analogous manner by the action of magnesium phenyl bromide (from 14 g. of bromobenzene) upon a solution of 4-methoxycoumarin (5 g.) in dry benzene (200 c.c.). The residue left after steam distillation was filtered off, dried, and twice recrystallised from absolute alcohol, the *chromen* being obtained in colourless plates, m. p. 135° (yield, 7 g.) (Found: C, 84·1; H, 5·5. $C_{22}H_{18}O_2$ requires C, 84·1; H, 5·7%). It is readily soluble in the usual organic solvents.

Hydrolysis.—The chromen (2 g.) was heated under reflux with 33% potassium hydroxide solution (25 c.c.) for 5 hours. After dilution with water, the whole was extracted with ether, and the oil isolated from the extract was treated with hydroxylamine. The solid thus obtained, after crystallisation from alcohol, melted at 139° and was shown to be identical with benzophenoneoxime by a mixed melting point with an authentic specimen.

4-Methoxy-2 : 2-dianisyl-Δ^3-chromen, prepared from magnesium *p*-anisyl bromide by the method previously described, crystallised from benzene in colourless needles, m. p. 155° (Found: C, 76·8; H, 6·0. $C_{24}H_{22}O_4$ requires C, 77·0; H, 5·9%).

2 : 2-Diphenyl-4-methyl-Δ^3-chromen (V).—This was prepared by treating a solution of 4-methylcoumarin (10 g.) in benzene (150 c.c.) with magnesium phenyl bromide (bromobenzene, 30 g.) in dry ether (100 c.c.). After boiling under reflux for 4 hours on the water-bath, the whole was steam-distilled and the residue extracted with ether. After removal of the solvent from the dried extract, crystals contaminated with some oily material were obtained. The oil was removed by treatment with a small quantity of alcohol, and the yellow solid recrystallised from benzene and again from glacial

acetic acid; the *chromen* then separated in colourless prisms, m. p. 89° (Found: C, 88·7; H, 6·4. $C_{22}H_{18}O$ requires C, 88·6; H, 6·1%).

Hydrolysis. Isolation of benzhydryl phenyl ether (VI). The above chromen (0·5 g.) was gently boiled under reflux with 50% potassium hydroxide solution (15 c.c.) for 24 hours. After cooling, the reaction mixture was extracted with ether. The oil left after removal of the solvent from the washed and dried extract solidified on standing and then crystallised from a very small volume of light petroleum in colourless needles, m. p. 56°. The compound was insoluble in aqueous sodium hydroxide and gave no colour reaction with ferric chloride (Found: C, 88·0; H, 6·4. $C_{19}H_{16}O$ requires C, 87·8; H, 6·2%).

2 : 2-*Diphenyl*-4 : 6-*dimethyl*-Δ^3-*chromen*.—The Grignard reaction in this case was carried out in a similar manner to that described by Löwenbein (*loc. cit.*) by the slow addition of magnesium phenyl bromide (from bromobenzene, 14 g.) to a hot solution of 4 : 6-dimethylcoumarin (5 g.) in benzene (120 c.c.). The reaction mixture was then heated on the water-bath for ½ hour, decomposed by means of cold ammonium chloride solution, and steam-distilled to remove bromobenzene and diphenyl. The residue, which became solid after 24 hours, was then separated and rubbed with a small quantity of ether, which induced it to crystallise. The product was recrystallised from alcohol, separating in colourless rhombs, m. p. 126°. The ether used to crystallise the residue from the steam distillation deposited more of the same compound (Found: C, 88·3; H, 6·5. $C_{23}H_{20}O$ requires C, 88·4; H, 6·4%).

Hydrolysis. Isolation of benzhydryl p-*tolyl ether*. The chromen (2 g.) was gently boiled under reflux with potassium hydroxide solution (25 g. in 25 c.c. of water) for 24 hours. After cooling, the yellow, alkaline solution, together with some solid material, was extracted with ether, and the extract was well washed with water, dried, and evaporated. The residual solid crystallised from 90% alcohol (animal charcoal) in colourless rhombs, m. p. 96°, which were insoluble in sodium hydroxide solution (Found: C, 87·8; H, 5·9. $C_{20}H_{18}O$ requires C, 87·6; H, 5·8%).

Diphenyl-2-*hydroxy*-β : 4-*dimethylstyrylcarbinol* (XIII).—4 : 7-Dimethylcoumarin was treated with magnesium phenyl bromide as was the 4 : 6-isomeride. The resinous product from the steam distillation was dried between porous tiles and then vigorously scratched with ether, whereupon it crystallised. The crystalline mass so obtained was filtered off and twice recrystallised from 90% alcohol, from which the *carbinol* separated in colourless needles, m. p. 146° (yield, 10%) (Found: C, 83·4; H, 6·4. $C_{23}H_{22}O_2$ requires C, 83·6; H, 6·6%).

2 : 2-*Diphenyl*-4 : 7-*dimethyl*-Δ^3-*chromen*.—This compound was obtained in two ways : (*a*) The ethereal filtrate after removal of the preceding carbinol deposited, on slow evaporation, a large quantity of a solid, which crystallised from alcohol in colourless needles, m. p. 86° (yield, 75%). (*b*) Diphenyl-2-hydroxy-β : 4-dimethylstyrylcarbinol (1 g.) was heated under reflux for 1 hour with glacial acetic acid (20 c.c.). The gummy residue obtained on dilution with water was crystallised from alcohol, yielding glistening, colourless needles, m. p. 87°, identical with the product in (*a*) (Found : C, 88·3; H, 6·7. $C_{23}H_{20}O$ requires C, 88·4; H, 6·5%).

Isolation of Benzhydryl m-*Tolyl Ether*.—This hydrolysis was carried out in three ways : (*a*) As in previous cases, the chromen (2 g.) was heated for 24 hours with potassium hydroxide solution (25 g. in 25 c.c. of water). The crude product crystallised from alcohol in colourless needles, m. p. 125°. (*b*) The chromen (2 g.) was heated with potassium hydroxide (15 g. in 25 c.c. of water) at 180° in an autoclave for 4 hours. The product was washed with water (200 c.c.), and the solid crystallised twice from 75% alcohol in presence of animal charcoal. It was thus obtained in colourless needles identical with those in (*a*). (*c*) The chromen (1 g.) was fused with potassium hydroxide (10 g.) and, when cold, the mass was dissolved in water and extracted with ether. After purification, the substance described in (*a*) and (*b*) was obtained (Found : C, 87·4; H, 5·9. $C_{20}H_{18}O$ requires C, 87·6; H, 5·8%).

The alkaline solution from (*c*) was rendered acid, and the solution, which contained a small quantity of solid material, was extracted with ether. After removal of the solvent, the residue crystallised from a small volume of methyl alcohol in colourless needles, m. p. 103—105°. It readily reduced Fehling's solution and Tollens's reagent and was identical with lactaldehyde in all respects.

2 : 4-*Diphenyl*-3-*methylchroman*-2-*ol*.—3-Methylcoumarin (10 g.), dissolved in benzene, was heated for 4 hours on the water-bath with magnesium phenyl bromide (3 mols.). The reaction mixture was decomposed with dilute hydrochloric acid and steam-distilled. The non-volatile residue was collected and crystallised from alcohol and finally from benzene, from which the *chromanol* separated in colourless crystals, m. p. 149° (Found : C, 83·9; H, 6·1. $C_{22}H_{20}O_2$ requires C, 83·5; H, 6·3%).

2 : 4-*Diphenyl*-3-*methyl*-Δ^2-*chromen* was prepared by boiling the above chromanol (1·5 g.) with glacial acetic acid (10 c.c.) for 1 hour. The cold solution was diluted with water, and the precipitate crystallised from alcohol, the *chromen* separating in colourless needles, m. p. 91° (Found : C, 88·5; H, 6·2. $C_{22}H_{18}O$ requires C, 88·6; H, 6·1%).

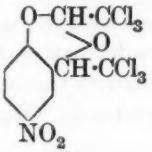
In conclusion, we desire to express our thanks to the Council of the Department of Scientific and Industrial Research for a grant to one of us (D. W. H.) which has enabled this research to be carried out.

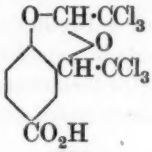
THE UNIVERSITY, LIVERPOOL. [*Received, June 8th*, 1927.]

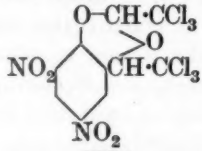
CCLXV.—*The Condensation of Chloral with Phenol.*

By FREDERICK DANIEL CHATTAWAY and ALEXANDER ALLAN MORRIS.

IT has been shown recently (J., 1926, 2720; this vol., p. 685) that in presence of concentrated sulphuric acid, chloral reacts readily with *p*-nitrophenol and with *p*-hydroxybenzoic acid, yielding respectively anhydro-5-nitro- (I) and anhydro-5-carboxy-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene (II)


(I.)

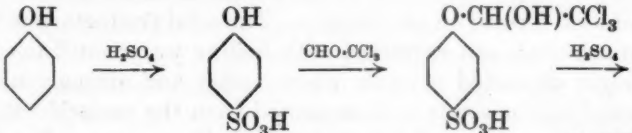

(II.)

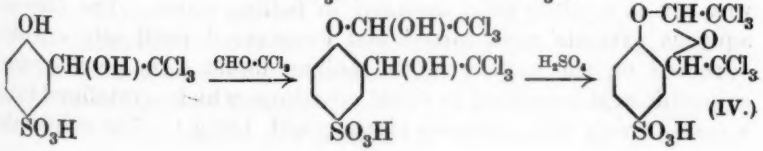

(III.)

Chloral appears to condense in this way only with phenols in which the hydrogen in the para-position to the hydroxyl has been replaced by other groups.

When phenol itself is added to chloral suspended in concentrated sulphuric acid, an immediate reaction occurs, and an oily liquid separates which rapidly changes into an opaque, white solid. This readily dissolves in alcohol, giving a colourless solution from which nothing crystallises on cooling. On evaporating off the solvent, a viscid liquid is left which solidifies to a colourless, transparent, resin-like mass, the constitution of which has not yet been determined.

If, however, the phenol is first dissolved in the sulphuric acid, whereby *p*-phenolsulphonic acid is formed, this on addition of chloral slowly reacts, forming a compound (IV) analogous in structure to the above (I and II).



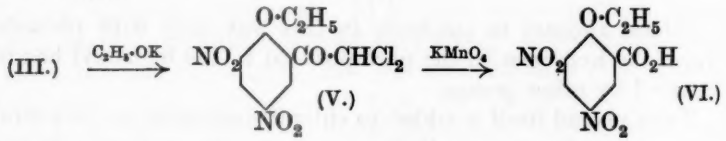

(IV.)

This compound behaves in all respects as a normal sulphonic acid. It is a colourless solid with no definite melting point. It crystallises with three molecules of water, two of which can be removed by heating, and forms well-crystallised salts. When acted upon by phosphorus pentachloride, it forms a *sulphonyl chloride*. This with ethyl and methyl alcohol yields *esters*, with ammonia a *sulphonamide*, and with aniline a *sulphonanilide*.

Its constitution is similar to that of the condensation product (I) yielded by *p*-nitrophenol, since both compounds on nitration yield *anhydro*-3 : 5-*dinitro*-2-βββ-*trichloro*-α-*hydroxyethoxy*-1-βββ-*trichloro*-α-*hydroxyethylbenzene* (III).

The molecules of water are probably attached to the sulphonic residue, the anhydride ring remaining unbroken, since, although only two are removed by heating, yet the ammonium salt is obtained in the anhydrous condition.

The constitution of the acid is further confirmed by the product of the action of alcoholic potash on the dinitro-derivative (III), whereby ωω-*dichloro*-3 : 5-*dinitro*-2-*ethoxyacetophenone* (V) is formed, which on oxidation by potassium permanganate yields 3 : 5-dinitro-2-ethoxybenzoic acid (VI).



Experimental.

Anhydro-2-βββ-*trichloro*-α-*hydroxyethoxy*-1-βββ-*trichloro*-α-*hydroxyethylbenzene*-5-*sulphonic Acid* (IV).—Phenol (100 g.; 1 mol.) was added slowly to 1000 c.c. of well-cooled sulphuric acid (*d* 1·8). After an hour, 400 g. of chloral hydrate (2 mols. + 50 g. excess) were gradually added with constant stirring. The mixture was then kept at the ordinary temperature for 4 days with occasional vigorous shaking. Reaction slowly took place, a bulky, white solid separating in the body of the solution, whilst a solid crust of metachloral formed on the surface. The solid products were filtered off on asbestos, and extracted with boiling water until the filtrate no longer deposited crystals when cooled and strongly acidified. The *sulphonic acid* was thus separated from the metachloral, which was left as a white solid insoluble in boiling water. The filtered aqueous extracts were mixed and evaporated until oily streaks appeared on the surface of the boiling liquid. On cooling, the sulphonic acid separated in viscid oily drops which crystallised into a mass of very thin, lustrous plates (yield, 150 g.). The sulphonic

acid is moderately easily soluble in boiling benzene and separates from this solution in very thin, colourless, lustrous, irregular plates containing three molecules of water (Found: C, 23·75; H, 2·3; Cl, 42·2. $C_{10}H_6O_5Cl_6S,3H_2O$ requires C, 23·8; H, 2·4; Cl, 42·1%).

When heated, the trihydrated acid partly liquefies between 125° and 130°, small prismatic crystals of a monohydrated acid separating.

When heated for ½ hour at 110°, the acid loses two molecules of water, leaving a crystalline aggregate of small, colourless, prismatic crystals of the monohydrated acid (Found: Loss of water at 110°, 7·0. $C_{10}H_6O_5Cl_6S,3H_2O \longrightarrow H_2O$ requires loss of water, 7·1%).

The monohydrated acid is very easily soluble in alcohol and acetone, and very sparingly soluble in boiling benzene and chloroform. It can be recrystallised by dissolving it in boiling acetic acid and adding concentrated hydrochloric acid a little at a time until the solution shows a slight turbidity. On cooling, the acid separates in small, colourless prisms which melt with decomposition between 150° and 166° (Found: C, 25·5; H, 1·7; Cl, 45·3; S, 7·0. $C_{10}H_6O_5Cl_6S,H_2O$ requires C, 25·6; H, 1·7; Cl, 45·4; S, 6·85%).

When moistened with a little cold water, the crystals of the monohydrated acid swell up into an amorphous sticky mass, which on warming gives a clear solution from which the hydrated acid crystallises on addition of a little concentrated hydrochloric acid.

It forms an anhydrous *ammonium* salt which crystallises from a dilute aqueous solution of ammonia in very small, colourless prisms (Found: C, 25·9; H, 2·0; Cl, 45·5. $C_{10}H_9O_5NCl_6S$ requires C, 25·65; H, 1·9; Cl, 45·5%).

Nitration of Anhydro-2-ββδ-trichloro-α-hydroxyethoxy-1-ββδ-trichloro-α-hydroxyethylbenzene-5-sulphonic Acid.—The sulphonic acid (40 g.) was added to a mixture of 150 c.c. of nitric acid (*d* 1·5) and 5 c.c. of concentrated sulphuric acid and heated to boiling. After cooling, the brown solution was poured on crushed ice; the dinitro-compound (III) then separated as a greenish-white solid, which, after drying, was recrystallised from boiling alcohol.

A product similar in every way was obtained when anhydro-5-nitro-2-ββδ-trichloro-α-hydroxyethoxy-1-ββδ-trichloro-α-hydroxyethylbenzene was nitrated in the same manner.

Anhydro-3:5-dinitro-2-ββδ-trichloro-α-hydroxyethoxy-1-ββδ-trichloro-α-hydroxyethylbenzene (III) is easily soluble in boiling acetic acid, alcohol, acetone, and benzene, and crystallises from all these solvents in two polymorphic modifications. On cooling, a solution of the compound in about three times its weight of boiling alcohol the labile modification first separates as slender, silky needles. On allowing these to stand in the mother-liquor, pale yellow rhombohedra of the stable form appear and grow at the expense of the labile form,

which dissolves and finally disappears. Both forms melt at 163° (Found: N, 6·0; Cl, 46·1. $C_{10}H_4O_6N_2Cl_6$ requires N, 6·1; Cl, 46·2%).

The position of the second nitro-group in this compound was established by its behaviour with alcoholic potash. The finely powdered dinitro-compound (25 g.) was gradually added to a solution of 30 g. of potassium hydroxide in 400 c.c. of alcohol, well cooled in a freezing mixture; it dissolved, giving a deep red solution, and chloroform was produced. After about 15 minutes, the liquid was neutralised by hydrochloric acid and the alcohol distilled off in a current of steam; *ωω-dichloro-3 : 5-dinitro-2-ethoxyacetophenone* (V) then separated as a liquid, which on cooling solidified to a crystalline, yellow mass (17·5 g.). It is readily soluble in boiling alcohol, from which it separates in small, yellow prisms, m. p. 82—84°, which darken when exposed to strong sunlight (Found: N, 8·7; Cl, 22·2. $C_{10}H_8O_6N_2Cl_2$ requires N, 8·7; Cl, 22·0%).

It yields an *osazone*,

$$OEt\cdot C_6H_2(NO_2)_2\cdot C(:N\cdot NH\cdot C_6H_3Cl_2)\cdot CH:N\cdot NH\cdot C_6H_3Cl_2,$$

when heated with an alcoholic solution of 3 : 5-dichlorophenylhydrazine. This compound is very sparingly soluble in boiling chloroform, from which it separates in minute, orange needles, m. p. 224° (Found: N, 14·4; Cl, 24·6. $C_{22}H_{16}O_5N_6Cl_4$ requires N, 14·3; Cl, 24·2%).

Oxidation of ωω-Dichloro-3 : 5-dinitro-2-ethoxyacetophenone by Permanganate.—ωω-Dichloro-3 : 5-dinitro-2-ethoxyacetophenone (15 g.) was added to a hot aqueous solution of 15 g. of potassium permanganate, and boiled until the oily drops first formed on the addition of the compound disappeared. The deep yellow filtrate from the precipitated manganese dioxide was concentrated, and an excess of hydrochloric acid added; 3 : 5-dinitro-2-ethoxybenzoic acid then separated, m. p. 132·5° (compare Ullmann, *Annalen*, 1909, **336**, 85) (Found: C, 42·6; H, 3·3; N, 10·9. Calc. for $C_9H_8O_7N_2$: C, 42·2; H, 3·1; N, 10·9%).

Anhydro-2-βββ-trichloro-α-hydroxyethoxy-1-βββ-trichloro-α-hydroxyethylbenzene-5-sulphonyl Chloride, $O<\begin{matrix}CH(CCl_3)\cdot O\\CH(CCl_3)\end{matrix}>C_6H_3\cdot SO_2Cl$.—The monohydrated acid (30 g.) and powdered phosphorus pentachloride (55 g.) were heated on the water-bath for 5 minutes, and the viscous pale brown oil formed was poured slowly over crushed ice. The *sulphonyl chloride* separated as a white solid, and crystallised from ether–light petroleum in very slender, colourless needles, m. p. 130·5° (Found: C, 25·5; H, 1·3; Cl, 52·6. $C_{10}H_5O_4Cl_7S$ requires C, 25·6; H, 1·1; Cl, 52·9%).

When boiled with any alcohol it reacts readily and yields the corresponding alkyl sulphonate. The *methyl* ester separates from

boiling methyl alcohol, in which it is moderately easily soluble, in small, highly refracting, colourless prisms, m. p. 150° (Found : C, 28·3; H, 1·7; Cl, 45·7. $C_{11}H_8O_5Cl_6S$ requires C, 28·4; H, 1·7; Cl, 45·8%). The *ethyl* ester separates from boiling ethyl alcohol in small, colourless, elongated, irregular plates, m. p. 143° (Found : C, 29·4; H, 2·2; Cl, 44·5. $C_{12}H_{10}O_5Cl_6S$ requires C, 30·1; H, 2·1; Cl, 44·4%).

The sulphonyl chloride also reacts readily with ammonia and with aniline in boiling alcohol to form a sulphonamide and a sulphonanilide.

Anhydro-2-βββ-*trichloro*-α-*hydroxyethoxy*-1-βββ-*trichloro*-α-*hydroxyethylbenzene*-5-*sulphonamide* separates from boiling alcohol, in which it is readily soluble, in colourless, small, silvery plates, m. p. 207° (Found : N, 3·2; Cl, 47·3. $C_{10}H_7O_4NCl_6S$ requires N, 3·1; Cl, 47·3%).

When dissolved in acetic acid and chlorinated, it yields *anhydro*-2-βββ-*trichloro*-α-*hydroxyethoxy*-1-βββ-*trichloro*-α-*hydroxyethylbenzene*-5-*sulphondichloroamide*, which dissolves easily in chloroform and separates in colourless, slender prisms, m. p. 165—174° (decomp.) (Found : Cl as $\cdot NCl_2$, 13·4. $C_{10}H_5O_4NCl_8S$ requires Cl as NCl_2, 13·7%).

Anhydro-2-βββ-*trichloro*-α-*hydroxyethoxy*-1-βββ-*trichloro*-α-*hydroxyethylbenzene*-5-*sulphonanilide* crystallises from dilute alcohol in very slender, silky, hair-like prisms, m. p. 168·5° (Found : N, 2·7; Cl, 40·5. $C_{16}H_{11}O_4NCl_6S$ requires N, 2·7; Cl, 40·5).

THE QUEEN'S COLLEGE, OXFORD. [*Received June 24th*, 1927.]

NOTES

Co-ordination Compounds of Beryllium and m- *and* p-*Nitrobenzoylacetone.* By HENRY BURGESS.

THE mutarotation of beryllium benzoylcamphor was attributed to an asymmetric arrangement around the beryllium atom by Lowry and Burgess (J., 1924, **125**, 2082), but owing to the occurrence of two asymmetric carbon atoms in the camphor nucleus, rigorous proof of the suggestion could not be obtained. It was proposed to confirm it by using an unsymmetrical β-diketone or β-ketonic ester which contained no asymmetric carbon atom and the basic or acidic group necessary for the resolution. *p*- and *m*-Aminobenzoylacetone and ethyl *p*-nitrobenzylacetoacetate appeared to fulfil these conditions. Owing to the resolution of beryllium benzoylpyruvate by Mills and Gotts (J., 1926, 3121), it was decided to place on record the results already obtained.

p-*Nitrobenzoylacetone.*—Freshly powdered sodamide (10·5 g.) was

slowly added to ethyl *p*-nitrobenzoate (50 g.) and acetone (19·8 c.c.) in dry ether (150 c.c.), cooled to −17°. The mixture immediately became greenish-black and ammonia was evolved. After being kept for 2 hours in the freezing mixture and for 20 hours at room temperature, the product was poured into ice-water, the ether separated, and the aqueous layer extracted twice with chloroform. (From these extractions, 16 g. of ethyl *p*-nitrobenzoate were recovered.) The aqueous layer was filtered through charcoal and acidified, and the resulting precipitate was filtered off and dried. This solid was extracted several times with ether, the ethereal solution was evaporated, and the resulting yellowish-brown crystals were recrystallised from methyl alcohol (yield, 1·5 g.), p-*nitrobenzoylacetone* being obtained in golden-yellow needles, m. p. 112—113·5° (Found: C, 58·1; H, 4·5; N, 6·8. $C_{10}H_9O_4N$ requires C, 57·95; H, 4·4; N, 6·8%). It is readily soluble in ordinary organic solvents except the cold alcohols and is insoluble in water. With caustic soda, it gives a bright yellow solution, and with copper acetate it produces a green precipitate, which is soluble in chloroform.

Beryllium p-*nitrobenzoylacetone* was obtained in nearly theoretical yield by the method described for beryllium benzoylcamphor (*loc. cit.*) (Found: C, 57·6*; H, 3·9*; Be, 2·2*. $C_{20}H_{16}O_8N_2Be$ requires C, 57·0; H, 3·8; Be, 2·1%). It is readily soluble in chloroform and hot benzene, from which it separates in brownish-yellow, compact crystals, m. p. 243—244°. It is sparingly soluble in alcohol and insoluble in water.

m-*Nitrobenzoylacetone*.—Preliminary experiments having shown that benzoylacetone can be recovered quantitatively from concentrated sulphuric acid at room temperature, the following nitration was carried out: A mixture of nitric acid (*d* 1·42; 7 c.c.) and sulphuric acid (*d* 1·84; 24 c.c.) was slowly added to benzoylacetone (15 g.) in sulphuric acid (100 c.c.), mechanically stirred and kept at −11° to −9°. After 15 minutes, the product was poured on ice; the precipitate obtained crystallised from hot methyl alcohol in very pale yellow needles, m. p. 114—115° (*p*-nitrobenzoylacetone depresses the m. p. by 20°) (yield, 47%) (Found: C, 58·1; H, 4·6%). m-*Nitrobenzoylacetone* is easily soluble in ordinary organic solvents except the cold alcohols and ligroin. The yellow coloration with alkalis is less intense than that of the *p*-nitro-derivative. With alcoholic ferric chloride, it gives a wine-red colour.

Beryllium m-*nitrobenzoylacetone*, prepared by the usual method, crystallised from acetone–alcohol in orange-yellow, square plates, m. p. 207—208° (Found: C, 57·3*; H, 3·9*; Be, 2·1%). It is

* Values so marked are the results of micro-estimations carried out by Siegmund Weil, Tübingen.

readily soluble in chloroform and benzene, less soluble in acetone, and slightly soluble in alcohol.

Ethyl Bis-p-*nitrobenzylacetoacetate.*—*p*-Nitrobenzyl bromide was slowly added to an equivalent quantity of ethyl sodioacetoacetate in absolute alcohol, sodium bromide being precipitated. After heating for 2 hours, the alcohol was evaporated, water added, and the precipitate crystallised from acetone–methylated spirit, *ethyl bis*-p-*nitrobenzylacetoacetate* separating in colourless flakes, m. p. 137—139° (Found: C, 60·5, 60·0; H, 5·0, 4·6; N, 6·8, 6·7. $C_{20}H_{20}O_7N_2$ requires C, 60·0; H, 5·0; N, 7·0%). It is readily soluble in acetone, ether, chloroform, and hot benzene, and sparingly soluble in cold alcohol. It gives a coloration neither with caustic soda nor with ferric chloride.

Ethyl p-*Nitrobenzylacetoacetate.*—The mother-liquor from the above compound left an orange-coloured oil on evaporation. This solidified when cooled in the ice-chest, and crystallised from benzene–ligroin in very pale yellow needles, m. p. 43—45° (Found: C, 59·05; H, 5·8. $C_{13}H_{15}O_5N$ requires C, 58·8; H, 5·7%). It is very soluble in all organic solvents except ligroin, in which it is sparingly soluble. With caustic soda, it gives an intense yellowish-orange coloration, and with ferric chloride a deep reddish-purple colour slowly develops. Copper acetate precipitates a green copper derivative, which is soluble in chloroform.

I wish to take this opportunity of expressing my thanks to the Chemical Society for a grant towards the expenses of the research, and also to Professor C. S. Gibson for his helpful criticism and encouragement.—Guy's Hospital Medical School. [*Received, March 21st*, 1927.]

The Reduction of Arsenic Compounds in Acid and in Alkaline Solution by Sodium Hyposulphite (*Hydrosulphite*). *Production of Sodium Arseno-hyposulphite.* By Walter Farmer and James Brierley Firth.

In an investigation on the reduction of certain arsenic compounds by sodium hyposulphite, in which a product corresponding to arsenic subsulphide, As_3S, was isolated (J., 1926, 119), it was inferred from preliminary experiments (and existing literature) that two intermediate complex compounds are formed, one of which is a decomposition product of the other.

The Primary Intermediate Complex, Sodium Arseno-hyposulphite, $Na_3As(S_2O_4)_3$.—Preliminary experiments carried out in glass vessels indicated that, in the presence of alcohol, shaking of an alkaline solution of trisodium arsenite containing hyposulphite was followed

by formation of two unstable precipitates, one of which was heavier than the other. Similar heavy precipitates were obtained when concentrated solutions of common sodium arsenate were used.

The products adhered to the walls of the vessel, and became viscous when treated with dilute alcoholic potash. In subsequent experiments, quartz containers were employed.

Sodium hyposulphite (2·75 g.) was introduced into a cold solution of 2·75 g. of common sodium arsenate in 3 c.c. of water to which a whirling motion had been imparted. The flask was closed, and the whirling maintained. Dissolution of the last traces of sodium hyposulphite was accompanied by formation of a heavy, granular solid, which settled in increasing quantity when the flask was kept at room temperature. The supernatant liquor was decanted off after 15 minutes, and the granular solid was washed five times by decantation with methylated alcohol and four times with benzene and kept in a quartz dish in a vacuum over sulphuric acid for 24 hours. A creamy-white powder was obtained (yield, 1 g.).

When a small quantity of the product was strongly heated in a Bunsen flame, a brown and a yellow sublimate formed and a garlic odour developed. If cautiously heated, the product first turned brown and, when more strongly heated, gave a brown and a yellow sublimate as before. When a small quantity of the product was treated with dilute hydrochloric acid, sulphur dioxide was evolved, and a brown product similar to that described in the previous paper (*loc. cit.*) formed.

Estimations of the arsenic content of the product, as magnesium pyroarsenate, gave: As, 14·1, 14·1, 14·1, 14·0%. Estimations of hyposulphite by Wilkes's method (*J. Soc. Chem. Ind.*, 1923, **42**, 356T) were based on the view that, in presence of hypoiodous acid, hydrolysis of 1 g.-mol. of arseno-hyposulphurous acid, $H_3As(S_2O_4)_3$, is attended by liberation of 4 g.-mols. of iodine according to the following equations:

(1) $H_3As(S_2O_4)_3 + 3H_2O = H_3AsO_3 + 3H_2S_2O_4$,
(2) $H_3AsO_3 + 2HIO + 3KOH = I_2 + K_3AsO_4 + 4H_2O$,
(3) $3H_2S_2O_4 + 9KIO + 6KOH = 6KHSO_4 + 9KI + 3H_2O$,
(4) $6KHSO_4 + 3KIO + 3KI = 3I_2 + 6K_2SO_4 + 3H_2O$.

Two samples gave: S_2O_4, 70·9, 70·5 [$Na_3As(S_2O_4)_3$ requires As, 14·2; S_2O_4, 72·7%].

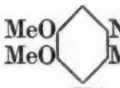
The Secondary Intermediate Complex, Sodium Arseno-thiosulphate, $Na_3As(S_2O_3)_3$.—Standard solutions of potassium hydroxide and hydrochloric acid of the same normality were prepared. 25 C.c. of the standard alkali in which 1 g. of sodium arseno-hyposulphite (1 mol.) and the calculated quantity of sodium sulphite (3 mols.)

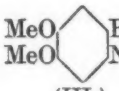
had been dissolved were rapidly added to 25 c.c. of the standard acid containing 2·5 c.c. of concentrated acid. A turbidity developed, followed by precipitation of arsenious sulphide. Decomposition of sodium arseno-hyposulphite in presence of sodium sulphite by this neutralisation method is considered to lead to formation, and rapid decomposition, of sodium arseno-thiosulphate, arsenious sulphide being one of the products (compare Jellinek, *Z. physikal. Chem.*, 1911, **76**, 257; Szilàgyi, *Z. anorg. Chem.*, 1920, **113**, 69).—University College, Nottingham. [*Received, April 8th*, 1927.]

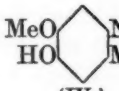
The Displacement of Bromine accompanying the Nitration of 6-Bromo homoveratrole. By Tom Heap, Thomas G. H. Jones, and Robert Robinson.

Jones and Robinson (J., 1917, **111**, 919) described the conversion of 6-bromohomoveratrole (I) into a mononitro-derivative, m. p. 121°, by the action of a mixture of nitric acid and acetic anhydride.

(I.)


(II.)


(III.)


(IV.)

We have, however, been unable to repeat the preparation of the nitro-derivative, since, on several occasions, following the description as closely as possible, the sole product of a sluggish reaction was 6-nitrohomoveratrole (II) (yield, 36%). Although it may be that some variation of the conditions is responsible for this divergence, we think it more likely that the observation of Jones and Robinson was erroneous as the result of contamination of the creosol employed with guaiacol and that the compound isolated was 4-bromo-5-nitroveratrole (III), m. p. 124° (or 121—122°, see below).

It is no longer necessary to employ beechwood tar as a source of creosol, since the pure phenol can be readily obtained from vanillin by Clemmensen's method.

6-*Bromohomoveratrole* (I).—The reduction of vanillin (100 g.) by means of amalgamated zinc and hydrochloric acid (Oberlin, *Arch. Pharm.*, 1925, **263**, 641) gave creosol (60 g.), b. p. 220—225°/760 mm., which was converted by known methods into homoveratrole, b. p. 218—220°, m. p. 22° (yield, 91%), and then into 6-bromohomoveratrole, b. p. 265—267°, m. p. 31° (yield, 94%). The latter crystallised in truncated octahedra, and, on oxidation with potassium permanganate and boiling dilute aqueous sodium hydroxide for 1½ hours, yielded 6-bromoveratric acid; this, alone or mixed with a specimen obtained by brominating methyl veratrate and hydrolys-

ing the product, melted at 183—184°. When treated with a mixture of acetic anhydride and nitric acid under the conditions prescribed by Jones and Robinson (*loc. cit.*), bromohomoveratrole (20 g.) gave 6-nitrohomoveratrole (8·5 g.), which crystallised in yellow needles from methyl alcohol; m. p. 117—119°, alone or mixed with an authentic specimen (Found: C, 55·0; H, 5·8. Calc. for $C_9H_{11}O_4N$: C, 54·8; H, 5·6%).

6-*Nitroisocreosol* (IV).—Cardwell and Robinson (J., 1915, **107**, 256) commented on the fact that 6-nitrohomoveratrole is not readily hydrolysed by alkalis. It is certainly less readily attacked than nitroveratrole, but by following the procedure of Pollecoff and Robinson (J., 1918, **113**, 647) for the preparation of 4-nitroguaiacol an almost theoretical yield of the nitro*iso*creosol was obtained in 73 hours. The substance crystallised from aqueous alcohol in slender, pale yellow needles, m. p. 168—170° (Found: C, 52·6; H, 4·6; N, 7·6. $C_8H_9O_4N$ requires C, 52·5; H, 4·9; N, 7·7%). The *acetyl* derivative crystallised from alcohol in colourless, elongated, hexagonal plates, m. p. 100—101°. On methylation the phenol yielded 6-nitrohomoveratrole, m. p. 117—119°. The conditions applicable for its further nitration to 2 : 6-dinitro*iso*creosol were not ascertained, since the action of nitric acid led to the production of soluble orange-red substances.

6-*Bromoveratric Acid*.—When methyl veratrate is brominated in cold acetic acid solution and the product crystallised, the yield of pure methyl 6-bromoveratrate, m. p. 88—89°, is not satisfactory, and Professor Smiles has suggested to us that methyl 2-bromoveratrate may be produced in the reaction. On treatment with cold nitric acid (*d* 1·42) pure 6-bromoveratric acid, m. p. 183—184°, gave a 50% yield of 4-bromo-5-nitroveratrole, m. p. 121—122°, whilst the crude product gave a 36% yield of this substance under identical conditions. 4-Bromo-5-nitroveratrole, prepared from bromoveratrole, had m. p. 121—122°, and a mixture with the specimen from 6-bromoveratric acid had the same m. p. The matter will be further investigated, our chief concern at the moment being to confirm the recorded m. p.'s of 6-bromoveratric acid and its methyl ester.—THE UNIVERSITY, MANCHESTER. [*Received, July 11th*, 1927.]